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# PATENT ABSTRACTS OF JAPAN

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## (54) PRODUCTION OF FILM STRUCTURE, ELECTRONIC DEVICE, RECORDING MEDIUM AND FERROELECTRIC THIN FILM

### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a film structure with a ferroelectric thin film having a relatively low dielectric constant, high residual polarization and low polarization reversal voltage and less liable to deterioration even after repeated polarization reversal by using a PbTiO<sub>3</sub>-base compsn. contg. a specified rare earth element.

SOLUTION: This ferroelectric thin film formed on a substrate contains R1 (R1 is one or more among Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd and Er or these elements and La), Pb, Ti and O and has a perovskite type crystal structure and single (001) orientation or (001) orientation and (100) orientation. The atomic ratio of (Pb+R1) to Ti is 0.8-1.3 and that of Pb to (Pb+R1) is 0.5-0.99. This thin film is obtd. by carrying out vapor deposition using at least lead oxide and TiO<sub>x</sub> ( $1 \leq x \leq 1.9$ ) as evaporating sources while introducing oxidizing gas into a reaction chamber when a ferroelectric thin film made of oxide contg. at least Pb and Ti is formed on a substrate by a multiple vapor deposition method.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the membrane structure object containing a ferroelectric thin film, the electron device equipped with this membrane structure object, the record medium using this membrane structure object, and the method of manufacturing a ferroelectric thin film by plural vacuum depositions. The aforementioned membrane structure object is applied to the record medium which is made to carry out polarization reversal of the ferroelectric with various electron devices, such as non-volatile memory which built the ferroelectric into the semiconductor device, an infrared sensor, an optical modulator, an optical switch, and OEIC (opto-electronic integrated circuit : opto-electronic integrated circuits), or an AFM (atomic force microscope) probe, and records information.

[0002]

[Description of the Prior Art] The electron device which formed the dielectric thin film on Si substrate which is a semiconducting-crystal substrate, and was integrated is devised. The dielectric separation LSI by still higher LSI of a degree of integration and SOI technology is considered by combining a semiconductor and a dielectric. Moreover, the ferroelectric which is a kind of a dielectric is applicable to non-volatile memory by using polarization reversal, and since an infrared sensor, an optical modulator, optical-switch OEIC, etc. can be constituted, examination of a ferroelectric thin film material is advanced energetically. Moreover, application to the record medium with which a ferroelectric thin film records information using the polarization reversal by the AFM probe etc. is also considered. In the non-volatile memory and the record medium using polarization reversal of a ferroelectric, as a ferroelectric thin film material, a remanence value is large and what bears the repeat of record and read-out is needed.

[0003] Although the memory of the structure which used the ferroelectric for the gate of FET is devised as one sort of non-volatile memory, the memory which uses a ferroelectric for the gate has plentifully the point which should problem-etc.-solve the problem on production, and ferroelectric physical properties of thin film, and has not resulted in utilization as stated to electronic-intelligence communication society issue Shingaku Giho, SDM 93-136, ICD 93-130, (1993-11), and 53 pages. By this type of memory, although it is ideal to make a memory cell into metal-ferroelectric-semiconductor (MFS) structure, since realization is difficult, generally it considers as metal-ferroelectric-insulator-semiconductor (MFIS) structure or metal-ferroelectric-metal-insulator-semiconductor (MFMIS) structure. In such structures, in order to carry out polarization reversal of the ferroelectric and to carry out memory operation, you have to apply the electric field of sufficient intensity for a ferroelectric. With MFIS structure and MFMIS structure, since a ferroelectric and an insulator become equivalent to the series connection of a capacitor, in order to apply electric field to a ferroelectric enough, the device which lowers the dielectric constant of a ferroelectric and gathers the dielectric constant of an insulator is needed.

[0004] as the material of a present and ferroelectric thin film -- lead system oxides, such as PbTiO<sub>3</sub>,

PZT (PbZrO<sub>3</sub>-PbTiO<sub>3</sub> system), and PLZT (PbZrO<sub>3</sub>-PbTiO<sub>3</sub> system by which La<sub>2</sub>O<sub>3</sub> was added), and Bi<sub>2</sub>Ti<sub>2</sub>NbO<sub>9</sub> etc. -- it inquires by the polarization property excellent in Bi system oxide being shown [0005] However, since a dielectric constant will become high about with 1000 if it thin-film-izes, when it uses as a ferroelectric thin film in the above-mentioned MFIS structure and above-mentioned MFMIS structure, it is difficult for PZT or PLZT to impress sufficient voltage.

[0006] On the other hand, it is PbTiO<sub>3</sub>. The dielectric constant in bulk is as small as about [ 100 or less ] at a room temperature, and spontaneous polarization is 80microC/cm<sup>2</sup> at the theoretical value of a bulk crystal. Compared with the material of other composition, a big value is shown wonderfully, and the Curie point is as high as 500 degrees C. That is, the most ideal value is indicated by the collection of data when thinking as a ferroelectric material of a memory use. Moreover, PbTiO<sub>3</sub> Even when it thin-film-izes, a dielectric constant is about 500 and a low. However, PbTiO<sub>3</sub> Various troubles are becoming clear as a result of furthering the research and development which thin-film-ize and are made into an electron device. the voltage Ec which carries out polarization reversal in the first place -- 85 kV/cm the defatigation property by polarization reversal, i.e., a repeat property, being bad to that leak arises in a thin film by being too high, the second crystal defect, semiconductor-ization, etc., and the third, and deteriorating in about 1000 times -- it comes out

[0007] In order to acquire a ferroelectric property, it is necessary to make it crystallize in the thin film material of the above-mentioned lead system oxide or Bi system oxide. the method of heating the temperature under thin film formation at 600 degrees C or more in order to make it crystallizing, and the method of annealing above 600 degrees C after membrane formation -- Jpn.J.Appl.Phys. -- 31, 3029 (1992), and Jpn.J.Appl.Phys. -- 33, 5244 (1994), and Mat.Res.Soc.Sympo.Proc. -- it is indicated by 243, 473 (1993), etc. However, Pb and Bi have high vapor pressure also in any of a metal and an oxide, and in order that they may evaporate in hot heat treatment and may cause a composition gap, a difficulty is in composition control.

[0008] Generally, in order to secure the device property optimal as a ferroelectric material, and its repeatability, it is desirable to use a single crystal. In the polycrystalline substance, it is difficult to obtain a good device property because of the disturbance of the physical quantity by the grain boundary. This is the same also about a thin film material, and a ferroelectric epitaxial film near the most perfect possible single crystal is desired. The same is said of the ferroelectric thin film in the non-volatile memory of the above-mentioned MFIS structure or MFMIS structure, and to be a dielectric epitaxial film near the most perfect possible single crystal is desired. Moreover, also in the medium (usually MFIS structure or MFMIS structure) which records using probes, such as AFM and STM, since the writing of a high-density bit will be attained if the ferroelectric epitaxial film near the most perfect possible single crystal is used, the realization is desired. Although it is necessary to grow epitaxially a metal thin film and a ferroelectric thin film on Si substrate which is a semiconductor substrate in order to realize a ferroelectric epitaxial film with MFIS structure or MFMIS structure, now, it does not realize yet.

[0009] With the ferroelectric material of a lead system, there is no composition gap and the thin film more near a single crystal is not obtained on the semiconductor substrate until now. Moreover, the ferroelectric material of a lead system of reactivity with Si used as a substrate will also be high, and it will have serious influence for the integrated-circuit property produced in Si substrate by diffusion of Pb to Si substrate.

[0010]

[Problem(s) to be Solved by the Invention] this invention is made in order to conquer the trouble mentioned above. The purpose of this invention is offering the membrane structure object which has a ferroelectric thin film with little degradation, even if a dielectric constant is comparatively low, a remanence is large, and a polarization turn over voltage is low and repeats polarization reversal. Moreover, other purposes of this invention have the fixed composition which was impossible until now, and are offering the method a crystalline high lead system ferroelectric thin film's being manufactured.

[0011]

[Means for Solving the Problem] The above-mentioned purpose is attained by one composition of

following the (1) - (18).

- (1) It is the membrane structure object which has a substrate and the ferroelectric thin film formed on this substrate, and a ferroelectric thin film is R1 (R1). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, and Er, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of  $(\text{Pb}+\text{R1})/\text{Ti}=0.8-1.3$  and  $\text{Pb}/(\text{Pb}+\text{R1})=0.5-0.99$ . The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled.
- (2) The membrane structure object of the above (1) with which the ferroelectric thin film is formed in the aforementioned front-face side of the substrate which has Si (100) side on a front face.
- (3) It is the membrane structure object which has a substrate and the ferroelectric thin film formed on this substrate, the front face by the side of the ferroelectric thin film of a substrate has Si (100) side, and a ferroelectric thin film is R2 (R2). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, Er, and La, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of  $(\text{Pb}+\text{R2})/\text{Ti}=0.8-1.3$  and  $\text{Pb}/(\text{Pb}+\text{R2})=0.5-0.99$ . The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled.
- (4) It is one membrane structure object of above-mentioned (1) - (3) which it has an insulating ground thin film between a substrate and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, is single (001) orientation when it is a tetragonal phase, and is single (100) orientation when it is a cubic.
- (5) It is the membrane structure object of above-mentioned (1) - (3) which is single (100) orientation when it has a middle thin film and this middle thin film makes a principal component the zirconium oxide by which this zirconium-oxide system thin film was stabilized by a zirconium oxide or rare earth elements (Sc and Y are included) including the zirconium-oxide system thin film, and it is single (001) orientation when it is a tetragonal phase or monoclinic system and it is a cubic, while a substrate and a ferroelectric thin film.
- (6) It is the membrane structure object of the above (5) which this rare earth oxide system thin film exists [ a middle thin film ] between a zirconium-oxide system thin film and a ferroelectric thin film including a rare earth oxide system thin film, and this rare earth oxide system thin film makes a principal component the oxide of rare earth elements (Sc and Y are included), is single (001) orientation when it is a tetragonal phase or monoclinic system, and is single (100) orientation when it is a cubic.
- (7) It is the above (5) or the membrane structure object of (6) which it has an insulating ground thin film between a middle thin film and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, is single (001) orientation when it is a tetragonal phase, and is single (100) orientation when it is a cubic.
- In contact with a ferroelectric thin film, it has a conductive ground thin film. (8) This conductive ground thin film It is the conductive oxide thin film which consisted of oxides which have the oxide or the perovskite type crystal structure containing the conductive metal thin film which consisted of at least one sort of Pt, Ir, Os, Re, Pd, Rh, and Ru, and/or In. It is one membrane structure object of above-mentioned (1) - (7) which is single (001) orientation when it is a tetragonal phase, and is single (100) orientation when it is a cubic.
- (9) a ferroelectric -- a thin film -- a front face -- at least -- 80 -- % -- a field -- setting -- criteria -- length -- 500 -- nm -- ten -- a point -- the average of roughness height --  $R_z$  -- ten -- nm -- less than -- it is -- the above -- (-- one --) -- (-- eight --) -- either -- a membrane structure -- the body .
- (10) One membrane structure object of above-mentioned (1) - (9) with which below 60 atom % of Ti in a ferroelectric thin film is replaced by at least one sort of Zr, Nb, Ta, Hf, and Ce.
- (11) The above (1) Electron device which has one membrane structure object of - (10).
- (12) The above (1) Record medium which has one membrane structure object of - (10).
- (13) The manufacture method of the ferroelectric thin film which performs vacuum evaporatio while facing the ferroelectric thin film which consists of an oxide which contains Pb and Ti at least forming on a substrate by plural vacuum depositions and introducing a oxidizing gas in a vacuum evaporatio

reaction chamber at least, using a lead oxide and  $\text{TiO}_x$  ( $1 \leq x \leq 1.9$ ) as an evaporation source.

(14) It is the atomic ratio of the element supplied from an evaporation source  $\text{Pb/Ti} = E$  ( $\text{Pb/Ti}$ ) It is an atomic ratio in the ferroelectric thin film which were formed by carrying out  $\text{Pb/Ti} = F$  ( $\text{Pb/Ti}$ ) The manufacture method of the ferroelectric thin film the above (13) set to  $E (\text{Pb/Ti}) / F (\text{Pb/Ti}) = 1.5-3.5$  when it carries out.

(15) The above (13) using the oxygen which at least the part radical-ized as a oxidizing gas, or the manufacture method of the ferroelectric thin film of (14).

(16) The manufacture method of one ferroelectric thin film of above-mentioned (13) - (15) which makes temperature of a substrate 500-700 degrees C, and performs vacuum evaporation.

(17) The manufacture method of one ferroelectric thin film of above-mentioned (13) - (16) that the ferroelectric thin film containing at least one sort of Zr, Nb, Ta, Hf, and Ce is formed.

(18) The manufacture method of one ferroelectric thin film of above-mentioned (1) above-mentioned [ which is applied to manufacture of one membrane structure object of - (10) ] (13) - (17).

[0012]

[Function of the Invention] At this invention, it is  $\text{PbTiO}_3$  as composition of a ferroelectric thin film. What added predetermined rare earth elements is used for system composition.  $\text{PbTiO}_3$  Although spontaneous polarization, a dielectric constant, and the Curie point are suitable for memory, there are troubles, like that the voltage  $E_c$  which carries out polarization reversal is too high, that leak arises in a thin film, and the defatigation property by polarization reversal is bad. The above trouble was solved by this invention.

[0013] In this invention, they are rare earth elements at a predetermined ratio  $\text{PbTiO}_3$  By adding,  $E_c$  was reduced and, moreover, it made it possible to suppress reduction of the remanence value  $P_r$  accompanying it. Moreover, this invention persons investigated in detail the rare earth elements which are hard to produce semiconductor-ization, and realized the ferroelectric thin film with little leak. It traced having influenced the fatigue property of polarization reversal of the kind and amount of rare earth elements to add simultaneously, and the ferroelectric thin film which was excellent in the repeat property was realized.

[0014] Specifically, in this invention, Pb, Ti, and O are contained as a ferroelectric thin film, and it is the above R2 at the above R1 and the second mode in the first mode further. What is contained is used. In the second mode, La is increasing as alternative of rare earth elements to the first mode.

[0015] The ferroelectric thin film in the first mode is single (001) orientation, or orientation (001) and orientation (100) are intermingled. Since it has such orientation, the property as a ferroelectric thin film becomes good, especially leak decreases.

[0016] In addition, adding Sc, Y, run TANOINDO, etc. like the first mode into the oxide ferroelectric material containing Pb and Ti is indicated by JP,7-94608,A. In the example of this official report, the ferroelectric thin film is formed by the spatter on Si (110) substrate. In a spatter target, it is  $\text{Y}_2\text{O}_3$ . Included  $\text{PbTiO}_3$  It uses. In this official report, since the ferroelectric thin film is formed by such method, the above-mentioned orientation in the first mode is not realized, but it is thought that it is in the state near a polycrystal film. A remanence value will become small if crystallinity is bad. In the example of this official report, it is making to suppress reduction of the remanence value by the repeat of fatigue by polarization reversal, i.e., polarization reversal, into the effect. However, since it has the small remanence value that fatigue by polarization reversal becomes small in this official report, it is thought that it originates in the stress produced by polarization reversal having become small. Though the above-mentioned fatigue is suppressed when a remanence value is small, it cannot be said that it is practical.

[0017] Moreover, the ferroelectric material of the lead-titanate system which added Sm or Gd used in the first mode is indicated by JP,7-202039,A. In this official report, the laminating of a titanium-nitride layer and the platinum layer was turned up, and the ferroelectric layer is formed. As the formation method of a ferroelectric layer, a spatter, CVD, the sol-gel method, and the laser abrasion method are mentioned, and the sol-gel method is explained as an example. When multilayer structure and the formation method given [ this ] in an official report are used, the ferroelectric thin film of the above-mentioned orientation in the first mode cannot be formed, and, naturally the effect in the first mode is

not realized, either.

[0018] Moreover, the ferroelectric material of the titanate-acid lead zirconate system which added Er used in the first mode is indicated by JP,7-73732,A. However, in this official report, the sol-gel method is mentioned as the formation method of a ferroelectric thin film. In a sol-gel method, the ferroelectric thin film of the above-mentioned orientation in the first mode cannot be formed, and, naturally the effect in the first mode is not realized, either.

[0019] In the second mode, the front face by the side of a ferroelectric thin film uses what has Si (100) side as a substrate in which a ferroelectric thin film is formed. According to the experiment of this invention persons, it is  $\text{TiO}(\text{Pb}, \text{La})_3$ . Although there is no leak and the polarization turn over voltage  $E_c$  becomes low when a thin film is formed on Si (100) substrate, when it forms, for example on a  $\text{MgO}$  (100) substrate, there will be much leak and  $E_c$  will become high. For this reason, Si (100) substrate is used in the second mode. Moreover, there is also a merit which is mentioned later in Si substrate.

[0020] The ferroelectric thin film of a lead-titanate system or a titanate-acid lead zirconate system which added La used in the second mode is indicated by JP,59-138004,A, a 60-172103 official report, a 62-252005 official report, a 62-252006 official report, a 4-199745 official report, JP,3-35249,B, etc.

[0021] Although some in which orientation (001) and orientation (100) were intermingled are in the ferroelectric thin film indicated by these official reports, there is nothing that could form such an orientation film on Si (100) substrate like the second mode, and it uses the  $\text{MgO}$  (100) substrate altogether. Although the above-mentioned orientation can be attained comparatively easily if a  $\text{MgO}$  (100) substrate is used, since the coefficient of thermal expansion is larger than Si, in case it is cooled to a room temperature after formation, big stress will arise in a ferroelectric thin film, and, thereby, the leak of  $\text{MgO}$  will increase remarkably. In addition, it is thought that it is because it is observed as it is easy to be extended in the direction where the crystal lattice of a ferroelectric thin film is perpendicular to a substrate side in order it has a large substrate that the above-mentioned orientation can be attained comparatively easily [ when a  $\text{MgO}$  (100) substrate is used ] and to contract, and c axis is carrying out orientation at right angles to a substrate side seemingly for this reason. When a ferroelectric thin film with a thickness of about 300nm is formed on a  $\text{MgO}$  substrate and the property is actually measured, compared with the amount of preferred orientation presumed from an X diffraction etc., only a low property is acquired remarkably but there is much especially leak remarkably. As for this, it is presumed to be the cause by contraction of a  $\text{MgO}$  substrate that a lot of residual stress in a ferroelectric thin film is accumulated.

[0022] Among the above-mentioned official reports, by JP,4-199745,A, as shown in the X diffraction view of a view 2, La addition lead-titanate thin film is formed on Si (100) substrate. However, in this thin film, only the peak by each side of (100), (110), and (111) is accepted, and it has not become orientation (001) so that clearly from a view 2. Although there was nothing that has formed La addition lead-titanate thin film of orientation (001) on Si (100) substrate conventionally, this is clear also from the publication of this official report.

[0023] Since the vapor pressure of Pb is high as compared with other elements when thin-film-izing the dielectric materials of Pb system, it is easy to cause a composition gap, and control of the amount of Pb (s) is difficult. With the ferroelectric material of Pb system, there is no composition gap and the thin film more near a single crystal is not obtained on the semiconductor substrate until now. In this invention, this property of Pb was used conversely and the optimum conditions of plural vacuum depositions were found out. On this condition, Pb is incorporated by the self-adjustment target the neither more nor less at a perovskite crystal, and the target ferroelectric crystal is obtained. Therefore, according to the manufacture method of this invention, crystalline high Pb system ferroelectric thin film is obtained, and, for this reason, outstanding strong dielectric characteristics are realized. Furthermore, on Si substrate, epitaxial growth becomes possible and it is very effective on electron device application. Moreover,  $\text{PbTiO}_3$  Since it is considering as the foundations of composition and a dielectric constant becomes comparatively low, it is suitable for memory application of the structure which used the ferroelectric for the gate of FET. The thin film optimal as an object for memory which applied MFIS structure and MFMS structure especially is obtained.



[0024]

[Embodiments of the Invention] The membrane structure object of this invention has at least a substrate and the ferroelectric thin film formed on this substrate. It is desirable that a middle thin film or an insulating ground thin film is prepared between a substrate and a ferroelectric thin film, and it is more desirable that the laminating is carried out in the order of a substrate, a middle thin film, an insulating ground thin film, and a ferroelectric thin film. Moreover, when preparing a conductive ground thin film, a conductive ground thin film is prepared in contact with a ferroelectric thin film. In this case, it is desirable that a middle thin film or an insulating ground thin film is prepared between a substrate and a conductive ground thin film, and it is more desirable that the laminating is carried out in the order of a substrate, a middle thin film, an insulating ground thin film, a conductive ground thin film, and a ferroelectric thin film. Hereafter, the manufacture method is explained to each thin film and a substrate row in detail.

[0025] Composition of the ferroelectric thin film which the membrane structure object of a <ferroelectric thin film> this invention has is  $\text{PbTiO}_3$ . Rare earth elements R1 predetermined to system composition Or R2 It adds. The following and R1 And R2 Rn It names generically.

[0026] Rn  $\text{PbTiO}_3$  It replaces by Pb located in A site of the basic perovskite which consists of material, and a crystal is made to transform.  $\text{PbTiO}_3$  A-axis: 3.904Å and c axis: 4.152Å It is a tetragonal phase type perovskite structure, and has a polarization shaft in c shaft orientations. Since this crystal deformation decreases the ratio of an a-axis and c axis, although it decreases spontaneous polarization slightly, it can reduce the voltage ( $E_c$ ) needed for the polarization reversal which poses a problem. On the other hand, it is Rn. It is  $\text{PbTiO}_3$  in the rare earth elements of an except, for example, Ce. Since it replaces by the element located in B site, and a crystal cannot be transformed effectively and spontaneous polarization falls extremely, it is not desirable to device application.

[0027] The ratios of the element in a ferroelectric thin film are  $(\text{Pb}+\text{Rn})/\text{Ti}=0.8-1.3$  and  $\text{Pb}/(\text{Pb}+\text{Rn})=0.5-0.99$ , and are  $/(\text{Pb}+\text{Rn}) \text{ Ti}=0.9-1.2$  and  $\text{Pb}/(\text{Pb}+\text{Rn})=0.7-0.97$  preferably. When  $(\text{Pb}+\text{Rn})/\text{Ti}$  is too small, it becomes impossible to desire a crystalline improvement effect, and if  $(\text{Pb}+\text{Rn})/\text{Ti}$  is too large, formation of a homogeneous thin film will become difficult. Moreover, good dielectric characteristics are obtained by making  $(\text{Pb}+\text{Rn})/\text{Ti}$  into the above-mentioned range. If  $\text{Pb}/(\text{Pb}+\text{Rn})$  is too small, while spontaneous polarization will become small, a dielectric constant will also become large or more with 1000. On the other hand, if  $\text{Pb}/(\text{Pb}+\text{Rn})$  is too large, the addition effect of rare earth elements, i.e., the fall effect of  $E_c$ , will become inadequate. It is easily realizable by controlling to mention the formation conditions of a ferroelectric thin film later to make  $\text{Pb}/(\text{Pb}+\text{Rn})$  into the above-mentioned range. Pb, Ti, and Rn It can ask for content by the X-ray fluorescence analysis.

[0028] A lead titanate is Rn added in this invention although it is generally  $\text{Pb}:\text{Ti}:\text{O}=1:1:3$ . The ratio of oxygen changes with a kind and amounts, and it is usually 2.7 to about 3.3.

[0029] As for a ferroelectric thin film, it is desirable to have the perovskite crystal structure and to have orientation at least (001). (001)  $\text{PbTiO}_3$  in which <001> shafts are perpendicular to the field inboard of a ferroelectric thin film, and have the crystal structure of a perovskite system in orientation Since the ferroelectricity of system material is acquired with <001> shafts, it is more desirable that a field (001) is a single (001) orientation film parallel in a film surface, and it is still more desirable that it is the epitaxial film defined in this specification. However, in this invention, orientation (100) with a field (100) parallel in a film surface may be intermingled. (100) Although an orientation crystal may form 90-degree domain and decreases spontaneous polarization slightly in this case, it does not become a serious obstacle. Moreover, since the stress in a thin film is decreased when 90-degree domain is formed, it is sometimes effective for improvement in a ferroelectric property. As for the peak intensity ratio in an X diffraction, it is usually desirable that (100)/(001) is three or less. In addition, even when orientation (100) is intermingled, it is desirable that it is the epitaxial film defined in this specification.

[0030] The desirable crystallographic-axis orientation relationship of the ferroelectric thin film in the case of using Si (100) substrate and Si substrate is as follows. In addition, Si is a cubic. When the ferroelectric thin film of a perovskite structure is single (001) orientation, they are perovskite [100]// Si [010]. Moreover, when orientation (001) and orientation (100) are intermingled, ferroelectric thin films

are perovskite [100]// Si [010] about a perovskite (001) orientation crystal, and are perovskite [001]// Si [010] about a perovskite (100) orientation crystal. That is, as for a ferroelectric thin film and Si substrate, it is desirable that the shafts which exist in a field are parallel.

[0031] In addition, the single orientation film in this specification means the thing of the crystallization film with which the target crystal face is equal to a substrate front face and parallel. concrete -- for example, a single (001) orientation film, i.e., a c-th page single orientation film, -- 10% or less of the maximum peak intensity of the field (00L) reflection of reflectivity other than a field (00L) by membranous 2 theta-theta X diffraction (XRD) -- desirable -- 5% or less of thing -- it is . in addition, this specification -- setting (00L) -- etc. (002) etc. -- the display which names an equivalent field generically -- it is -- etc. (L00) etc. -- \*\*\*\*\* -- it is the same (001)

[0032] Moreover, when an epitaxial film makes the inside of a film surface a X-Y side and sets the Z-axis as the direction of thickness in this specification, the crystal is gathering and carrying out orientation to both the X-axis, a Y-axis, and Z shaft orientations. 10% or less of the maximum peak intensity of the field which the peak intensity of reflection of things other than the field made into the purpose specifically makes the purpose when measurement by the X diffraction is performed in the first place -- desirable -- 5% or less -- it is necessary to be . an epitaxial film (001), i.e., a c-th page epitaxial film, -- membranous 2 theta-theta X diffraction -- peak intensity other than a field (00L) -- 10% or less of the maximum peak intensity of a field (00L) -- desirable -- 5% or less -- it is . RHEED evaluation needs to show a spot or a streak pattern to the second. It can be called an epitaxial film if these conditions are satisfied. In addition, RHEED is a reflective high-speed electron diffraction (Reflection High Energy Electron Diffraction), and RHEED evaluation is the index of the orientation of the crystallographic axis in a film surface.

[0033] Although a part of Ti in a ferroelectric thin film may be replaced by at least one sort of Zr, Nb, Ta, Hf, and Ce, as for the substitutional rate of Ti by these elements, it is desirable that it is below 60 atom %. When a substitutional rate is too high, antiferroelectricity may be shown without becoming a ferroelectric. In addition, when Ti is replaced and above-mentioned (Pb+Rn) Ti is computed, these substitution elements are converted into Ti and considered.

[0034] Although especially the material of the substrate used by the <substrate> this invention is not limited, a single crystal is used preferably. Specifically, although any, such as semiconductors, such as insulators, such as a magnesia, a strontium titanate, sapphire, a zirconia, a stabilized zirconia, a lithium niobate, and a lithium tantalate, and gallium arsenide, silicon, may be used, Si single crystal is used preferably. When it uses so that the field (100) of Si single crystal may turn into a substrate front face especially, the ferroelectric thin film which was excellent in the property can be formed. Moreover, since it is used widely by the semiconductor device, when composite-izing the membrane structure object of this invention with other elements, it is suitable, and since the coefficient-of-thermal-expansion coefficient of Si corresponds even when using it combining other elements, it is desirable. For example, since 1 figure of coefficients of thermal expansion of a MgO substrate differs from Si, they are unsuitable for such a use. Moreover, Si is comparatively cheap.

[0035] It is desirable to prepare an insulating ground thin film between a <insulating ground thin film> substrate and a ferroelectric thin film. In not preparing the conductive ground thin film mentioned later, an insulating ground thin film usually exists in contact with a ferroelectric thin film.

[0036] An insulating ground thin film has the perovskite crystal structure. A perovskite type structure is a chemical formula  $ABO_3$ . It is expressed. Here, A and B express a cation respectively. One or more sorts chosen from calcium, Ba, Sr, Pb, K, Na, Li, La, and Cd as A in this invention, especially Ba or Sr is desirable, and one or more sorts chosen from Ti, Zr, Ta, and Nb as B, especially Ti are desirable. That is, as for an insulating ground thin film, in this invention, it is desirable to form a barium titanate or a strontium titanate as a principal component.

[0037] atomic-ratio A/B in such a perovskite type compound -- desirable -- 0.8-1.3 -- it is 0.9-1.2 more preferably Less than by 0.8, if it becomes impossible to desire an improvement effect of crystallinity [ A/B ] and A/B exceeds 1.3, formation of a homogeneous thin film will become difficult. It can ask for the composition ratio of A/B from an X-ray fluorescence analysis.  $ABO_3$  Composition of O which can

be set is not limited to 3. Since there are some which construct the perovskite structure stabilized in an oxygen defect or hyperoxia depending on perovskite material, it is ABOX. It sets and, as for the value of  $x$ , it is desirable that it is 2.7-3.3.

[0038] It is desirable that the  $c$ -th page carries out orientation to single (001) orientation, i.e., a substrate front face, and parallel individually when it is a tetragonal phase, and when it is a cubic, it is desirable that the  $a$ -th page carries out orientation to single (100) orientation, i.e., a substrate front face, and parallel individually, and even when it is any, it is more desirable [ an insulating ground thin film ] that it is an epitaxial film. Moreover, as for the orientation relationship of an insulating ground thin film and Si (100) substrate, it is desirable that they are tetragonal [100]// Si [010], or cubic [010]//Si [010]. That is, as for a thin film and a substrate, it is desirable that shafts are parallel in a field. Such a laminated structure is effective for raising the crystallinity of the conductive ground thin film further formed on this structure, or a ferroelectric thin film, and forming these as a single orientation film or an epitaxial film. Since an insulating ground thin film has good grid adjustment with a ferroelectric thin film, a crystalline high ferroelectric thin film is obtained.

[0039] An insulating ground thin film functions also as an insulator in MFIS structure or MFMIS structure.

[0040] The conductive ground thin film prepared by sticking to a ferroelectric thin film between a <conductive ground thin film> substrate and a ferroelectric thin film functions as a lower electrode for constituting MFMIS structure required for the electrode for ferroelectric thin films, and memory application of a ferroelectric thin film.

[0041] Although it is desirable to consist of metals as for a conductive ground thin film, you may be the oxide and the conductive perovskite oxide containing In, and it is good also as composition which carried out the laminating of a metal membrane and the oxide film. As a metal, the metal simple substance and alloy containing at least one sort of Pt, Ir, Os, Re, Pd, Rh, and Ru are desirable. As the oxide containing In, or a conductive perovskite oxide,  $\text{In}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$  (Sn dope),  $\text{CoO}$  (R, Sr) $_3$ ,  $\text{RuO}$  (R, Sr, calcium) $_3$ ,  $\text{RuO}$  (R, Sr) $_3$ ,  $\text{SrRuO}_3$ ,  $\text{MnO(s)}$  (R, Sr) $_3$ , or these related compounds are desirable, for example. In addition, in the aforementioned compound, R is the rare earth elements containing Sc and Y.

[0042] Like an insulating ground thin film, when it is a tetragonal phase and they are single (001) orientation and a cubic, it is desirable that it is single (100) orientation, and even when it is any, as for a conductive ground thin film, it is more desirable that it is an epitaxial film. Moreover, as for the orientation relationship of a conductive ground thin film and Si (100) substrate, it is desirable that they are tetragonal [100]// Si [010], or cubic [010]//Si [010]. That is, as for a thin film and a substrate, it is desirable that shafts are parallel in a field. Such a laminated structure is effective for raising the crystallinity of the ferroelectric thin film further formed on this structure, and forming as a single orientation film or an epitaxial film. Since a conductive ground thin film has good grid adjustment with a ferroelectric thin film, a crystalline high ferroelectric thin film is obtained.

[0043] As for a conductive ground thin film, it is desirable that the specific resistance in bulk is  $10^{-5}$  -  $10^{-2}$  ohmcm. Moreover, as for the specific resistance as a thin film, it is desirable that they are  $10^{-5}$  -  $10^{-2}$  ohmcm. Moreover, the conductive ground thin film may consist of superconducting materials.

[0044] It is desirable that a middle thin film is prepared between a <middle thin film> substrate and a ferroelectric thin film. When preparing an insulating ground thin film, an insulating ground thin film will be located between a middle thin film and a ferroelectric thin film. A middle thin film consists of zirconium-oxide system thin films, or consists of this and a rare earth oxide system thin film. In addition, a rare earth oxide system thin film is prepared between a zirconium-oxide system thin film and a ferroelectric thin film. A middle thin film functions as an insulator in MFMIS structure or MFIS structure.

[0045] A zirconium-oxide system thin film zirconium-oxide system thin film makes a principal component the zirconium oxide (stabilized zirconia) which made the zirconium oxide the principal component or was stabilized by rare earth elements (Sc and Y are included). By preparing this thin film, ablation of the ground thin film prepared on it or a ferroelectric thin film can be prevented. Moreover,

since this thin film has good grid adjustment with the ground thin film which consists of a barium titanate etc., a crystalline high ferroelectric thin film is obtained as a result.

[0046] A zirconium oxide and a stabilized zirconia have the desirable thing of the composition expressed with  $Zr_{1-x}R_xO_{2-\delta}$  (R is the rare earth elements containing Sc and Y, and is  $x=0$  to  $0.75$ , and  $\delta=0-0.5$ ). About  $x$  and  $\delta$ , it mentions later. It is desirable that it is at least one sort chosen from Pr, Ce, Nd, Gd, Tb, Dy, Ho, and Er as R.

[0047] As for a zirconium-oxide system thin film, it is desirable to have single crystal orientation. Since a grain boundary exists in the thin film which has two or more crystal faces, this is because epitaxial growth of the ground thin film on it or a ferroelectric thin film becomes impossible. Specifically, when it is a tetragonal phase or monoclinic system and is single (001) orientation and a cubic, it is desirable that it is single (100) orientation, and even when it is any, it is more desirable that it is an epitaxial film. If such a good crystalline zirconium-oxide system thin film can be formed, the disturbance of the physical quantity by the grain boundary etc. will be lost, and a good insulating ground thin film, a conductive ground thin film, and a ferroelectric thin film will be obtained on a zirconium-oxide system thin film.

[0048] When the laminating of a middle thin film ( $Zr_{1-x}R_xO_{2-\delta}$ ) and the insulating ground thin film ( $BaTiO_3$ ) is carried out to Si (100) substrate front face one by one, these orientation relationships  $BaTiO_3/(001)/Zr_{1-x}R_xO_{2-\delta}(001)//Si(100)$ , and  $BaTiO_3$  It is desirable that they are  $[100]/Zr_{1-x}R_xO_{2-\delta}[100]/Si[010]$ . Although this is the case where each of middle thin films and insulating ground thin films is tetragonal phases, even when these thin films are cubics, it is the same at the point that it is desirable that shafts are parallel in a field.

[0049] By the analogy from the conventional examples, such as YBCO, it is  $BaTiO_3$  of orientation (001). When it is going to obtain an epitaxial film, the orientation relationship  $BaTiO_3/(001)/Zr_{1-x}R_xO_{2-\delta}(001)//Si(100)$ , And  $BaTiO_3$  It is set to  $[110]/Zr_{1-x}R_xO_{2-\delta}[100]/Si[010]$ , and is  $BaTiO_3$ . It is presumed that 45 degrees rotates within the c-th page to the grid of  $Zr_{1-x}R_xO_{2-\delta}$ , and a unit lattice can take adjustment of a grid, and grows epitaxially. However, according to the experiment of this invention persons, composition is difficult and such an orientation relationship is  $BaTiO_3/(001)/Zr_{1-x}R_xO_{2-\delta}(001)//Si(100)$ , and  $BaTiO_3$ . It found out that it could constitute from relation between  $[100]/Zr_{1-x}R_xO_{2-\delta}[100]/Si[010]$ .

[0050] Namely, the lattice constant of an a-axis is 0.52 by the  $Zr_{1-x}R_xO_{2-\delta}$  film, and is  $BaTiO_3$ .  $BaTiO_3$  which rotates and carries out grid adjustment in 45-degree side although it is 0.40 by the film In the relation between  $[110]/Zr_{1-x}R_xO_{2-\delta}[100]/Si[010]$ , misfit becomes 8.4%. However, grid adjustment relation  $BaTiO_3$  by this invention In  $[100]/Zr_{1-x}R_xO_{2-\delta}[100]/Si[010]$   $BaTiO_3$  The a-th page of a crystal and the a-th page of a  $Zr_{1-x}R_xO_{2-\delta}$  crystal are adjusted as they are, without rotating, and  $BaTiO_3$  4 grid ( $0.4 \times 4 = 1.60[nm]$ ) adjusts it to  $Zr_{1-x}R_xO_{2-\delta}$  3 grid ( $0.52 \times 3 = 1.56[nm]$ ) in this case. At this time, misfit is well matched with 2.6%. Therefore, at this invention, it is  $BaTiO_3$ . By using the relation between  $[100]/Zr_{1-x}R_xO_{2-\delta}[100]/Si[010]$ , it is epitaxial  $BaTiO_3$  of orientation (001). A film can be obtained.

[0051]  $ZrO_2$  It applies to a room temperature from an elevated temperature, and cubic  $\rightarrow$  tetragonal  $\rightarrow$  monoclinic system and phase transition are produced. It is the stabilized zirconia which added rare earth elements in order to stabilize a cubic. It depends for the crystallinity of a  $Zr_{1-x}R_xO_{2-\delta}$  film on the range of  $x$ . Jpn.J.Appl.Phys.27  $x$  becomes a tetragonal phase or a monoclinic system crystal in the composition region which is less than 0.2 as reported to (8) L1404-L1405 (1988). Until now, in two or more cubic fields, the epitaxial film of single orientation is obtained for  $x$ . However, although  $x$  is a cubic in the field exceeding 0.75, single orientation is not acquired but the crystal of orientation (111) mixes it, for example (100). On the other hand, in the field used as a tetragonal phase or monoclinic system, it is J.Appl.Phys.58. (6) Orientation sides other than what it is going to obtain mix, and the epitaxial film of single orientation is not obtained as stated also to 2407-2409 (1985).

[0052] Therefore, as for  $x$ , from the point of crystal orientation, it is desirable in  $Zr_{1-x}R_xO_{2-\delta}$  that it is 0.2-0.75. The more desirable ranges of  $x$  are 0.2-0.50. If a zirconium-oxide system thin film is an epitaxial film, it will be easy to grow epitaxially the insulating ground thin film and ferroelectric thin film which are formed on it.

[0053] In order for the rare earth elements which a stabilized zirconia contains to make the lattice constant of the thin film prepared on the lattice constant of Si substrate, and a zirconium-oxide system thin film, and the lattice constant of a zirconium-oxide system thin film match preferably, the kind and addition are chosen. For example, as for with an above-mentioned lattice constant of  $0.52\text{nm}$   $\text{Zr}_{1-x}\text{R}_x\text{O}_{2-\delta}$ , R is Y and x is the thing of 0.3. Although a lattice constant is changeable if x is changed with the kind of R fixed, the field of matching in change of only x which can be adjusted is narrow. When it changes to Y and Pr is used here, it is possible to enlarge a lattice constant and it is  $\text{BaTiO}_3$  of an insulating ground thin film. Matching with a crystal can be optimized.

[0054] In addition, the zirconium oxide which does not include an oxygen defect is a chemical formula  $\text{ZrO}_2$ . Although expressed, it becomes the range in which the amount of oxygen changed and usually described above  $\delta$  in  $\text{Zr}_{1-x}\text{R}_x\text{O}_{2-\delta}$  with the kind, amount, and valence of the rare earth elements which added the zirconium oxide which added rare earth elements.

[0055] In  $\text{Zr}_{1-x}\text{R}_x\text{O}_{2-\delta}$ , as mentioned above, crystallinity did not become fitness, and good front-face nature was not obtained in the field whose x is less than 0.2, and especially the composition region of a high grade where the ratio of Zr in the composition element except oxygen exceeds 93-mol%, either. However, as a result of this invention persons' repeating examination, by applying the manufacture method mentioned later showed the above-mentioned single orientation and that epitaxial growth became still more possible and a value also with good front-face nature was acquired.  $\text{ZrO}_2$  of a high grade There is a merit which is described below in a film.

[0056] It is  $\text{ZrO}_2$ , so that the ratio of Zr in the composition element except oxygen is high. It is desirable, when insulation resistance also becomes high and a leakage current also needs an insulating property from a bird clapper small so that purity is high. Moreover, it sets in metal-insulator-semiconductor structure (MIS structure), and is  $\text{ZrO}_2$ . Since the hysteresis of the C-V property of seeing when YSZ (Y stabilized zirconia) is used as an insulator is lost when it uses as an insulator, an interface property is excellent as an MIS element. As this reason, the stress generated by the difference in a coefficient of thermal expansion between Si substrate and a zirconium-oxide system thin film is  $\text{ZrO}_2$ . Being eased by phase transition and  $\text{ZrO}_2$  It is possible that there are few oxygen defects. Since stress was not eased since there was no phase transition, and YSZ has added rare earth elements, it has many oxygen defects. Moreover, it also sets in MFMS structure or MFIS structure, and is  $\text{ZrO}_2$  as an insulator. Since the C-V hysteresis of information-separator portion is lost when it uses, the C-V hysteresis by polarization reversal of a ferroelectric is acquired effectively, and is desirable.

[0057] therefore, the ratio of Zr in the composition element excluding the oxygen in a zirconium-oxide system thin film when good crystallinity and front-face nature are obtained -- desirable -- 93mol% \*\* -- more -- desirable -- more than 95mol% -- further -- desirable -- more than 98mol% -- it is more than 99.5mol% most preferably Oxygen and the composition element except Zr are usually rare earth elements, P, etc. In addition, now, the upper limit of the ratio of Zr is about 99.99mol%. Moreover, with the present high grade-ized technology, it is  $\text{ZrO}_2$ .  $\text{HfO}_2$  Since it is difficult, separation is  $\text{ZrO}_2$ . Purity has usually pointed out the purity in  $\text{Zr}+\text{Hf}$ . Therefore,  $\text{ZrO}_2$  in this specification Purity is  $\text{HfO}_2$  although it is the value computed by having considered that Hf and Zr were these elements. It sets to the zirconium-oxide system thin film in this invention, and is  $\text{ZrO}_2$ . Completely, in order to function similarly, it is satisfactory.

[0058] in addition, when forming a middle thin film, the oxygen in a middle thin film is spread near the substrate front face of Si single crystal substrate, and near a substrate front face oxidizes shallowly (for example, about 5nm or less) -- having --  $\text{SiO}_2$  etc. -- an oxidizing zone may be formed Moreover, depending on the method of membrane formation, Si oxide layer may remain on Si substrate front face at the time of middle thin film formation.

[0059] As the rare earth oxide system thin film above was carried out, when the stabilized zirconia described above as a middle thin film is used, a hysteresis is seen by the C-V property and it sets at this point, and it is  $\text{ZrO}_2$ . It is inferior to a high grade film. In this case, the hysteresis of a C-V property can be abolished by carrying out the laminating of the rare earth oxide system thin film on a zirconium-oxide system thin film. Moreover, matching of the grid adjustment between ferroelectric thin films

becomes better by carrying out the laminating of the rare earth oxide system thin film.

[0060] In addition, a rare earth oxide system thin film is formed on a zirconium-oxide system thin film because the film of single (001) orientation or single (100) orientation cannot be formed but it becomes the film of cubic orientation (111) only by the rare earth oxide system thin film.

[0061] As for a rare earth oxide system thin film, it is desirable to consist of substantially rare earth oxides of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu which contain at least one sort of Ce, Pr, Nd, Gd, Tb, Dy, Ho, and Er especially at least one sort. In addition, the ratio is arbitrary when using two or more sorts of rare earth elements.

[0062] When the laminating of the rare earth oxide system thin film is carried out, an element distribution may be a uniform film and a zirconium-oxide system thin film may be an inclination structure film from which composition changes in the direction of thickness. When considering as an inclination structure film, while applying to a rare earth oxide system thin film side from a substrate side and increasing gradually or gradually the rare-earth-elements content in a zirconium-oxide system thin film, Zr content is decreased gradually or gradually. By considering as such an inclination structure film, it becomes easy for the misfit of the grid between a zirconium-oxide system thin film and a rare earth oxide system thin film to become small, or to stop existing, and to make a rare earth oxide system thin film into the epitaxial film of high crystallinity.

[0063] In addition, as for the rare earth elements added to a rare earth oxide system thin film, it is desirable to use the same thing as the rare earth elements added to a zirconium-oxide system thin film.

[0064] You may introduce an additive into a zirconium-oxide system thin film and a rare earth oxide system thin film for a property improvement. For example, if alkaline-earth elements, such as calcium and Mg, are doped to these thin films, a membranous pinhole can decrease and leak can be suppressed. Moreover, aluminum and Si are effective in raising membranous resistivity. Furthermore, transition-metals elements, such as Mn, Fe, Co, and nickel, can form the level (trap level) by the impurity into a film, and conductive control is attained by using this level.

[0065] In order that a <crystallinity [ of each thin film ], front-face nature, and thickness> ground thin film and a middle thin film may raise the crystallinity of the thin film formed on it, its crystallinity is good and it is desirable that a front face is flat.

[0066] The half-value width of the rocking curve of the reflective peak in XRD (X diffraction) and the pattern of the image by RHEED can investigate the crystallinity of a thin film. Moreover, front-face nature can be investigated by the streak nature of a RHEED image, and the surface roughness (ten-point average of roughness height) measured by AFM.

[0067] As for the crystallinity of an insulating ground thin film, a conductive ground thin film, and a middle thin film, it is desirable that it is that from which the half-value width of the rocking curve of reflection of the field by the X diffraction (002) becomes 1.50 degrees or less. Moreover, about an insulating ground thin film and a middle thin film, when surface roughness  $R_z$  (the ten-point average of roughness height, a criteria length of 500nm) is measured by AFM, it is desirable that it is 2nm or less, and it is more desirable that it is 0.60nm or less. Moreover, as for the above  $R_z$  of a conductive ground thin film, it is desirable that it is 10nm or less. In addition, the front face of each thin film is desirable, and, as for such surface roughness, it is more preferably desirable to have realized in 95% or more of field still more preferably 90% or more 80% or more. The above-mentioned surface roughness is 2 an area of 10cm. When each thin film is formed over the whole substrate surface, it is the value which measures ten or more arbitrary places distributed over the average.

[0068] Although there are not half-value width of a rocking curve and especially a lower limit of  $R_z$ , and it is so desirable that it is small, now, the lower limit of the ten-point average of roughness height  $R_z$  with about 0.4 degrees and a criteria length of 500nm of the lower limit of the half-value width of a rocking curve is about 0.10nm.

[0069] A RHEED image is a streak, and moreover, when sharp, the crystallinity of each thin film and surface flat nature will be excellent.

[0070] The thickness of an insulating ground thin film changes with uses, and generally, although it is 50-150nm more preferably, it is preferably desirable that it is thin to the grade by which crystallinity and



front-face nature are not spoiled 5-500nm. Moreover, as for the thickness in the case of using an insulating ground thin film as an insulating layer, it is desirable that it is about 50-500nm.

[0071] The thickness of a conductive ground thin film also changes with uses, and generally, although it is about 50-150nm more preferably, it is preferably desirable that it is thin to the grade by which crystallinity and front-face nature are not spoiled 5-500nm. When operating a conductive ground thin film as an electrode layer, it is desirable to set thickness to about 50-500nm.

[0072] The thickness of a middle thin film also changes with uses, and generally, although it is 10-50nm more preferably, it is preferably desirable that it is thin to the grade which does not spoil crystallinity and front-face nature 5-500nm. Moreover, as for the thickness in the case of using a middle thin film as an insulating layer, it is desirable that it is about 50-500nm. In addition, when considering as the two-layer composition which described the middle thin film above, as for the thickness of each thin film, it is desirable that it is 0.5nm or more, and, as for the thickness of the whole middle thin film, considering as the above-mentioned range is desirable.

[0073] When a ferroelectric thin film front face is measured by AFM like the above, 10nm or less of  $R_z$  (es) with a criteria length of 500nm is 5nm or less more preferably. There is, and especially the lower limit of  $R_z$  is so desirable that it is small. [ no ] Since the capacity of memory is proportional to the number of bits when a ferroelectric thin film constitutes memory, in order to consider as a bulk memory, it is necessary to increase the number of bits per unit area. Since record becomes possible even if the front-face nature of a ferroelectric thin film carries out bit area to it being good small, the surface disposition top is effective at the point which increases the number of bits per unit area. Now, the lower limit of Above  $R_z$  is about 1nm.

➤ [0074] The membrane structure object of a <electron device> this invention is processed according to a semiconductor process, is constituted as the gate of a capacitor and FET, and let them be electron devices, such as non-volatile memory and an infrared sensor. Moreover, it is applicable to an optical modulator, an optical switch, OEIC, etc.

[0075] The membrane structure object of a <record-medium> this invention is applicable also to the record medium which records information with probes, such as AFM and STM (scanning tunneling microscope). The method of recording on a ferroelectric with probes, such as AFM, is indicated by JP,63-193349,A. On the occasion of record, first, voltage is impressed to a ferroelectric thin film with probes, such as AFM, and only the field by which the probe was carried out reverses polarization. The field by which polarization reversal was carried out serves as a record bit, and will support information. The piezoelectricity effect of a ferroelectric, a pyroelectric effect, the electro-optical effect, the current detection at the time of polarization reversal, etc. are used for read-out of information. Specifically, RF bias voltage is impressed to a record medium and a probe, and it scans with a probe. At this time, a record intermediation body surface deforms by the piezoelectricity effect of a ferroelectric thin film. Since the direction of polarization is reverse, piezoelectricity effects differ in a record bit field and a non-record section. For this reason, in a record-medium front face, the deformation according to existence of a record bit appears, and a record bit can be discriminated by detecting this deformation with a probe. What is necessary is to impress the pulse voltage of reversed polarity with the time of record, and just to reverse polarization, when eliminating a record bit.

[0076] In addition, the membrane structure object of this invention with which such a record reproduction method is applied is the thing of FMIS structure or FIS structure. Since it is necessary to impress electric field to a ferroelectric thin film at the time of record reproduction, in using the thing of FIS structure, generally it operates this as a lower electrode using a substrate with high conductivity.

[0077] Moreover, if the ferroelectric thin film is formed on Si substrate, capture of the charge by polarization reversal and a discharge phenomenon can be used, and a depletion layer can be formed by the charge captured by Si substrate which is a semiconductor. If such a depletion layer is formed, since capacity will change, it can consider as a record bit. Read-out in this case impresses RF bias voltage to a record medium and a probe like the above, and is performed by scanning with a probe. Since the field where charge capture is made differs in the capacity between a probe and a record medium from the field which is not made, a record bit is discriminable by detecting this capacity change. Elimination of a

record bit can be performed like the above.

[0078] In addition, by this record reproduction method, electric field are impressed through the semiconductor section, using the membrane structure object of FIS structure as a record medium.

[0079] AFM and STM have the resolution of atomic level. Moreover, since polarization reversal speed is as high-speed as 100 or less ns and it is possible to form a record bit with the size below 10nmphi, a ferroelectric is 2 100 megabits/cm. Realization of the above high-density memory is expected. In this invention, since the very good ferroelectric thin film of front-face nature is obtained, such high-density memory is realizable.

[0080] The <manufacture method of a ferroelectric thin film>, next the manufacture method of the ferroelectric thin film of this invention are explained in detail.

[0081] In addition, in enforcing the manufacture method of this invention, it is desirable to use vacuum evaporatono equipment 1 as shown in drawing 1 . Here, it is PbTiO<sub>3</sub> as a lead system ferroelectric thin film. Although the PGT thin film which is the composition which added Gd is mentioned as an example and explained, the thin film which consists of other lead system ferroelectric material can be manufactured similarly.

[0082] Vacuum evaporatono equipment 1 has vacuum tub 1a in which vacuum pump P was prepared, and the electrode holder 3 which holds a substrate 2 in the lower part is arranged in this vacuum tub 1a. It connects with the motor 5 through the axis of rotation 4, and can rotate by this motor 5, and this electrode holder 3 can rotate a substrate 2 now in the field. The above-mentioned electrode holder 3 builds in the heater 6 which heats a substrate 2.

[0083] vacuum evaporatono equipment 1 -- the oxidizing gas feeder 7 -- having -- \*\*\*\* -- the oxidizing gas feed hopper 8 of this oxidizing gas feeder 7 -- the above-mentioned electrode holder 3 -- it is arranged immediately below As for a oxidizing gas, the partial pressure is made high by about two substrate by this. In a lower part, they are the PbO evaporator 9 and TiO<sub>x</sub> to the pan of a electrode holder 3. The evaporator 10 and the rare-earth-elements evaporator 11 are arranged. The energy feeders (an electron ray generator, resistance heating equipment, etc.) for supplying the energy for evaporation other than each evaporation source are arranged at each [ these ] evaporator.

[0084] The reason using an oxide (PbO) as a lead evaporation source is that deposit efficiency will increase if PbO is used although it re-evaporates if Pb is used for an evaporation source and is hard to adhere to a substrate front face on a hot substrate, since the vapor pressure of Pb is high, and is TiO<sub>x</sub>. The reason for using is also that deposit efficiency is high similarly. TiO<sub>x</sub> When Ti is used instead, in order that Ti may tend to oxidize rather than PbO, since oxygen is taken by Ti, PbO serves as Pb and this re-evaporates it, it is not desirable.

[0085] in addition, TiO<sub>x</sub> x which can be set -- desirable --  $1 \leq x < 1.9$  -- more -- desirable --  $1 \leq x < 1.8$  -- further -- desirable --  $1.5 \leq x \leq 1.75$  -- it is  $1.66 \leq x \leq 1.75$  especially preferably Such TiO<sub>x</sub> If heat energy is applied, it will fuse within a vacuum tub and the stable vapor rate will be obtained. On the other hand, TiO<sub>2</sub> It is TiO<sub>x</sub>, emitting oxygen within a vacuum tub, if heat energy is applied. Since the vapor rate which the pressure fluctuation in a vacuum tub became large, and was stabilized in order to change is not obtained, composition control is impossible.

[0086] First, a substrate is set to the above-mentioned electrode holder. Although various kinds of things mentioned above can be used for substrate material, among these, Si single crystal substrate is desirable. It is desirable to use especially the field (100) of Si single crystal so that it may become a substrate front face. Moreover, it is also desirable to use as a substrate the single crystal board in which said middle thin film, the insulating ground thin film, the conductive ground thin film, etc. were formed.

[0087] By the manufacture method of this invention, it is a large area substrate, 10cm<sup>2</sup> [ for example, ], about a homogeneous ferroelectric thin film. It can form on a substrate with the above area. Thereby, let the electron device and record medium which have a ferroelectric thin film be a very cheap thing compared with the former. In addition, especially the upper limit of the area of a substrate is 2 400cm in the present condition, although there is nothing. It is a grade. Although the present semiconductor process has 2-8 inches Si wafer and a thing especially in use using the 6 inch type wafer, this invention can respond to this. Moreover, it is also possible not the whole wafer surface but to choose with a mask



etc. partially and to form a ferroelectric thin film.

[0088] Next, a substrate is heated in a vacuum and they are PbO and TiOx. And the ferroelectric thin film is formed by supplying Gd and a oxidizing gas to a substrate front face.

[0089] As for especially heating temperature, it is desirable to consider as 550-650 degrees C 500-700 degrees C. A crystalline high ferroelectric thin film is it hard to be obtained to be less than 500 degrees C. If it exceeds 700 degrees C, Si of a lead steam and a substrate etc. will react and a crystalline lead system ferroelectric film will be hard to be obtained. Moreover, when forming a ferroelectric thin film on conductive ground thin films, such as Pt, a reaction with Pt will arise.

[0090] As the above-mentioned oxidizing gas, although oxygen, ozone, atom-like oxygen, NO<sub>2</sub>, radical oxygen, etc. can be used, it is desirable to consider as the oxygen which radical-ized most most [ parts or ].

[0091] Here, the case where the radical oxygen by the source of efficient consumer response oxygen is used is explained.

[0092] Most supplies the radical-ized oxygen gas continuously in a vacuum deposition tub from the source of efficient consumer response oxygen, exhausting the inside of a vacuum tub continuously with a vacuum pump. As for oxygen tension [ near the substrate ], it is desirable that it is about 10<sup>-3</sup> to 10<sup>-1</sup> Torr. The upper limit of oxygen tension was set to 10<sup>-1</sup> Torr for keeping the vapor rate constant, without degrading the metal in the evaporation source in a vacuum tub. It faces introducing oxygen gas into a vacuum deposition tub, and gas is injected from the near on the surface of a substrate, it can be good to build the atmosphere of high oxygen tension only near the substrate, and, thereby, the reaction on a substrate can be promoted more in the few amount of gas introduction. Since the inside of a vacuum tub is continuously exhausted at this time, almost all the portions of a vacuum tub have a low pressure of 10<sup>-4</sup> - 10<sup>-6</sup> Torr. The amount of supply of oxygen gas is a part for 5-25 cc/preferably by 2-50 cc/. Since the optimal amount of supply of oxygen gas is decided by the capacity of a vacuum tub, and the factor of a pumping speed and others, it calculates the suitable amount of supply beforehand.

[0093] With an electron beam etc., each evaporation source is heated, is evaporated, and is supplied to a substrate. Membrane formation speed is 0.100 - 0.500 nm/s more preferably 0.05 to 1.00 nm/s. If membrane formation speed is too slow, it will become difficult to keep membrane formation speed constant, and a film will tend to become heterogeneous. On the other hand, if membrane formation speed is too quick, the crystallinity of the thin film formed is bad and irregularity will arise on a front face.

[0094] TiOx And what is necessary is just to supply it on a substrate with the vapor rate of the ratio corresponding to the composition ratio made into the purpose, since Gd is incorporated by the PGT crystal as which it supplied and as which the whole quantity grows on a substrate mostly. However, since vapor pressure is high, PbO tends to cause a composition gap, and control is difficult for it. With the ferroelectric material of a lead system, there is no composition gap and the thin film more near a single crystal is not obtained until now. In this invention, this property of PbO is used conversely and the amount-of-supply ratio to the substrate from a PbO evaporation source is made superfluous to the ratio in the PGT film crystal formed. atomic-ratio Pb/Ti=E (Pb/Ti) of Pb and Ti to which the degree of overage is supplied from an evaporation source Atomic-ratio Pb/Ti=F (Pb/Ti) of Pb and Ti in composition of the formed ferroelectric thin film, a relation --  $E (Pb/Ti)/F (Pb/Ti) = 1.5-3.5$  -- they are  $E (Pb/Ti)/F (Pb/Ti) = 1.7-2.5$  and the thing more preferably set to  $E (Pb/Ti)/F (Pb/Ti) = 1.9-2.3$  preferably PbO which is not included in superfluous PbO or a superfluous perovskite structure will be re-evaporated on a substrate front face, and only the PGT film of a perovskite structure will grow on a substrate.  $E (Pb/Ti)/F (Pb/Ti)$  If too small, it becomes difficult to fully supply Pb into a film, and the ratio of (Pb+Rn)/Ti in a film will become low too much, and will not serve as a crystalline high perovskite structure. On the other hand, it is  $E (Pb/Ti)/F (Pb/Ti)$ . If too large, the ratio of (Pb+Rn)/Ti in a film will become large too much, other Pb rich phases will appear besides a perovskite phase, and perovskite single phase structure will no longer be acquired.

[0095] As explained above, they are PbO and TiOx. By using as an evaporation source, raising deposit efficiency, and oxidizing powerfully by radical oxygen, and setting substrate temperature as the

predetermined range, the excess and deficiency of Pb twist and the PGT crystal of a stoichiometry grows up to be a self-adjustment target on a substrate mostly. This method is an epoch-making method of manufacturing the lead system perovskite crystal thin film of a stoichiometry, and a crystalline, very high ferroelectric thin film is obtained.

[0096] Membrane formation area is 2 10cm. When forming membranes on the front face of a substrate with a diameter of 2 inches when it is beyond a grade for example, oxidation reaction can be promoted throughout a membrane formation field by rotating a substrate, as shown in drawing 1, and supplying a oxidizing gas uniformly throughout a substrate front face. Thereby, moreover, formation of a homogeneous film is attained by the large area. At this time, the rotational frequency of a substrate is 10rpm. It is desirable that it is above. A rotational frequency tends to produce the distribution of thickness in a substrate side with a low. Especially the upper limit of the rotational frequency of a substrate is usually mechanism top 120rpm of vacuum devices, although there is nothing. It becomes a grade.

[0097] It is desirable after ferroelectric thin film formation to give annealing if needed. Preferably, 500-850 degrees C, annealing is 650-800 degrees C more preferably, and is performed for 5 - 15 minutes for [ for / 1 second / - ] 30 minutes. Although orientation (100) may appear (100) or the rate of orientation may increase when a ferroelectric thin film is annealed, generally the property as a ferroelectric improves by annealing. In addition, although it prepares an electrode layer on a ferroelectric thin film in considering as MFMIS structure or MFIS structure, in such a case, annealing may be performed before formation of an electrode layer and may be performed after formation. Since annealing is performed after crystallization, there are no worries about the composition gap by annealing.

[0098] As mentioned above, although the detail of the manufacture method of a ferroelectric thin film was explained, since this manufacture method can be enforced especially in comparison with the conventional vacuum deposition method, the sputtering method, the laser abrasion method, etc. under the operating condition which does not have the room of mediation of an impurity so that clearly and which is moreover easy to control, it is suitable to obtain the specified substance with good repeatability and high integrity by the large area.

[0099] Even if it furthermore uses MBE equipment in this method, the target thin film can completely be obtained similarly.

[0100] Although how to manufacture the thin film of the rare-earth-elements addition lead-titanate system which is the ferroelectric thin film which the membrane structure object of this invention has was described above, this method can be applied to PT system material which does not add rare earth elements, PZT system material, etc., and the same effect is acquired also by these cases. Moreover, it is applicable also to Bi system oxide thin film. Also in Bi system oxide thin film, since the vapor pressure of Bi was high, although composition control was inadequate in the vacuum until now, it sets by this invention method, and it is Bi  $2O_3$  about a PbO evaporation source. It is checking that it can manufacture similarly by changing to an evaporation source. It is incorporated by the self-adjustment target at a crystal that Bi is not in Bi system, and the ferroelectric thin film crystal of a stoichiometry is obtained.

[0101] The <manufacture method of a membrane structure object>, next the manufacture method of the membrane structure object of this invention are explained.

[0102] When using a substrate surface treatment Si single crystal substrate, it is desirable to perform surface treatment to a substrate before formation of a middle thin film. Below, the need for surface treatment is explained.

[0103] Generally the surface structure in the number atomic layer on the front face of a crystal differs from the atomic-arrangement structure of the imagination front face considered when the crystal structure of bulk (big 3-dimensional-like crystal) is cut. This is because the situation around the atom which appeared in the front face when the crystal of one side stopped there not being tends to change and it is going to be in the lower stable state of energy corresponding to this. The case where it stops at relief of an atomic position, and recombination of an atom mainly arise, and the structural change may form rearrangement structure. The former exists on almost all the crystal front face. Generally the latter

forms a superstructure in a front face. This is called  $m \times n$  structure, when setting the size of the unit vector of the surface structure of bulk to  $a$  and  $b$  and the superstructure of the size of  $ma$  and  $nb$  arises.

[0104] In order to grow an oxide thin film epitaxially on Si substrate, the structure of Si substrate front face is stable, and the role which Si substrate front face reports that the crystal structure information is to the oxide thin film to grow up must be played. Since the atomic-arrangement structure considered when the bulk crystal structure is cut is  $1 \times 1$  structure, the surface structure of the substrate for growing an oxide thin film epitaxially needs to be  $1 \times 1$  stable structure.

[0105] However, since the front face of Si (100) which it defecated serves as  $1 \times 2$  or  $2 \times 1$  structure so that it may mention later, and the front face of Si (111) becomes complicated super-structure with the big unit mesh of  $7 \times 7$  or  $2 \times 8$  structure, it is not desirable.

[0106] Moreover, these Si front faces that it defecated are rich in reactivity, the residual gas especially hydrocarbon, and reaction in a vacuum are caused, by forming SiC in a front face, a substrate front face is polluted especially with the temperature (700 degrees C or more) which carries out epitaxial formation of the oxide thin film, and a surface crystal is confused at it. Therefore, on the occasion of formation of an oxide thin film, it is necessary to protect Si front face which was rich in reactivity.

[0107] Since it is such, it is desirable to perform surface treatment to Si single crystal substrate by the following methods.

[0108] By this method, it sets to the electrode holder which shows Si single crystal substrate which defecated the front face first to drawing 1, and arranges in a vacuum tub, and it heats, introducing a oxidizing gas, and Si oxide layer is formed in a substrate front face. You may use air, although the thing same as a oxidizing gas as the case of the above-mentioned ferroelectric thin film can be used. Si oxide layer is for protecting a substrate front face from a rearrangement, contamination, etc. As for the thickness of Si oxide layer, it is desirable to be referred to as about 0.2-10nm. It is because protection of Si front face becomes imperfect for thickness to be less than 0.2nm. The reason for having set the upper limit to 10nm is mentioned later.

[0109] Grade maintenance is carried out for 0 - 10 minutes, and the above-mentioned heating is performed to the temperature of 300-700 degrees C. At this time, a programming rate is carried out in about 30-70 degrees C/minute. Conversely, temperature is too high, or if a programming rate is too quick, formation of Si oxide layer will become inadequate, and temperature will be too low, or if the holding time is too long, Si oxide layer will become thick too much.

[0110] When using oxygen as a oxidizing gas, as for introduction of a oxidizing gas, it is desirable that make the inside of a vacuum tub into the vacuum of about  $1 \times 10^{-7}$  to  $1 \times 10^{-4}$  Torrs at the beginning, and the oxygen tension in the atmosphere near the substrate carries out by [ as being set to  $1 \times 10^{-4}$  -  $1 \times 10^{-1}$  Torr ] at least by introduction of a oxidizing gas.

[0111] It heats in a vacuum after the above-mentioned process. Since Si crystal on the front face of a substrate is protected by Si oxide layer, it reacts with the hydrocarbon which is residual gas, and contamination of SiC being formed does not generate it. As for especially heating temperature, it is desirable to consider as 700-1100 degrees C 600-1200 degrees C.  $1 \times 1$  structure is not acquired on Si single crystal substrate front face as it is less than 600 degrees C. If it exceeds 1200 degrees C, protection of Si crystal by Si oxide layer becomes less enough, and the crystallinity of Si single crystal substrate will be confused.

[0112] Subsequently, Zr and a oxidizing gas, Zr and rare earth elements (Sc and Y are included), and a oxidizing gas are supplied to a substrate front face. In this process, metals, such as Zr, will return and remove Si oxide layer formed at the last process. The surface structure of  $1 \times 1$  is formed in Si crystal front face exposed simultaneously of Zr and oxygen or Zr, rare earth elements, and oxygen.

[0113] The pattern of the image by RHEED can investigate a surface structure. For example, in the case of the surface structure of  $1 \times 1$  which is desirable structure, the direction of electron ray incidence serves as a perfect streak pattern of the 1 time period C1 as shown in drawing 17 (a) by [110], and serves as the pattern completely same as for [1-10] in the direction of incidence. On the other hand, Si single crystal clean surface serves as a surface structure in which it is  $1 \times 2$  or  $2 \times 1$  in the case of a field (100), or  $1 \times 2$  and  $2 \times 1$  are intermingled. In such a case, the pattern of RHEED is the direction of incidence of an

electron ray [110], either of [1-10], or both, and turns into a pattern with the 1 time period C1 as shown in drawing 17 (b), and the double-precision period C2. In the surface structure of 1x1, it sees by the pattern of Above RHEED, and the directions of incidence are both [110] and [1-10], and the double-precision period C2 is not seen.

[0114] In addition, Si (100) clean surface may also show 1x1 structure, and our experiment was also observed several times. However, the conditions which show 1x1 are indefinite, and it is impossible in the present condition to obtain 1x1 with stably sufficient repeatability in respect of Si pure. 1x2, 2x1, and 1x1 -- even if it is the case of which structure, Si pure side is easy to be polluted with an elevated temperature among a vacuum, it reacts with the hydrocarbon contained especially in residual gas, SiC is formed, and the crystal on the front face of a substrate tends to be confused

[0115] As for Zr or Zr, and rare earth elements, it is desirable that the thickness when carrying out the vacuum evaporatio~~no~~ of these in an oxidizing atmosphere, and forming an oxide film supplies 0.3-10nm so that it may be especially set to about 3-7nm. The display of such the amount of supply is hereafter called amount of supply in oxide conversion. if the effect of reduction of Si oxide of the amount of supply in oxide conversion in less than 0.3nm cannot fully demonstrate but exceeds 10nm -- a front face -- the irregularity of atomic level -- generating -- being easy -- the array which is a surface crystal may be no longer 1x1 structure by irregularity The reason for having set the desirable value of the upper limit of the thickness of the above-mentioned Si oxide layer to 10nm is that possibility that it becomes impossible to fully return Si oxide layer will come out even if it supplies a metal as mentioned above if it exceeds 10nm.

[0116] When using oxygen as a oxidizing gas, it is desirable to supply about 2-50cc /a minute. Since the optimal amount of supply of a oxidizing gas is decided by the capacity of a vacuum tub, and the factor of a pumping speed and others, it calculates the optimal amount of supply beforehand.

[0117] As for a zirconium-oxide system thin film, it is desirable among the formation middle thin films of a middle thin film to form by the method which these people already proposed in Japanese Patent Application No. No. 93024 [ seven to ].

[0118] In formation of a thin film, a substrate is heated first. As for the heating temperature at the time of membrane formation, it is desirable that it is 400 degrees C or more because of crystallization of a zirconium oxide, and if it is 750 degrees C or more, in order to obtain the film excellent in crystallinity and to obtain the surface flat nature of molecule level especially, it is desirable that it is 850 degrees C or more. In addition, the upper limit of the heating temperature of a single crystal substrate is about 1300 degrees C.

[0119] Subsequently, while heating Zr, evaporating it with an electron beam etc. and supplying a substrate front face, rare earth elements are supplied to a substrate front face a oxidizing gas and if needed, and a zirconium-oxide system thin film is formed. Membrane formation speed is more preferably made into 0.100 - 0.500 nm/s 0.05 to 1.00 nm/s. If membrane formation speed is too slow, it will become difficult to keep membrane formation speed constant, on the other hand, if membrane formation speed is too quick, the crystallinity of the thin film formed will become bad and irregularity will arise on a front face.

[0120] In addition, about various conditions, such as oxygen tension the kind of oxidizing gas, its amount of supply, and near the substrate, and rotation of a substrate, it is the same as that of the case of the above-mentioned ferroelectric thin film formation.

[0121] What is necessary is to use only rare earth elements as an evaporation source, when carrying out the laminating of the rare earth oxide system thin film on a zirconium-oxide system thin film. The introductory conditions of the oxidizing gas at this time, the temperature conditions of a substrate, etc. are good like the case of a zirconium-oxide system thin film then. When using the same rare earth elements in both thin films, when a zirconium-oxide system thin film is formed in predetermined thickness, supply of Zr can be stopped, and a rare earth oxide system thin film can be continuously formed by supplying only the rare earth metal succeedingly. Moreover, what is necessary is to reduce the amount of supply of Zr gradually and just to shift to formation of a rare earth oxide system thin film as zero finally, in making a zirconium-oxide system thin film into inclination structure.

[0122] It is BaTiO<sub>3</sub> as an insulating ground thin film on an insulating ground thin film middle thin film. The case where a film is formed is explained.

[0123] Ba and Ti are supplied to a substrate front face after middle thin film membrane formation, continuing heating and introduction of an oxidizing gas. As for the amount of supply, it is desirable to make it set to Ba:Ti=1:1. The temperature of the vacuum evaporation substrate at the time of membrane formation and the Ba/Ti amount-of-supply ratio in early stages of membrane formation are BaTiO<sub>3</sub>. A membranous stacking tendency is affected. BaTiO<sub>3</sub> The orientation relationship of a film, a middle thin film (Zr<sub>1-x</sub>Rx O<sub>2-delta</sub>), and Si (100) substrate The desirable relation mentioned above, i.e., BaTiO<sub>3</sub>/(001)/Zr<sub>1-x</sub>Rx O<sub>2-delta</sub>(001)//Si, (100) And BaTiO<sub>3</sub> It is BaTiO<sub>3</sub> in order to make it set to [100]//Zr<sub>1-x</sub>Rx O<sub>2-delta</sub>[100]// Si [010]. The heating temperature at the time of membrane formation has preferably desirable 900-1200 degrees C 800-1300 degrees C. Moreover, it is desirable 1-0, and for the Ba/Ti amount-of-supply ratio in early stages of growth to set to 1-0.8 preferably. That is, it is desirable to \*\*\*\* to overTi in early stages of growth. In addition, it is shown that you may be it supply of only Ti that a Ba/Ti amount-of-supply ratio is 0 in early stages of growth. If heating temperature is too high, counter diffusion will arise in a thin film layered product, and crystallinity will fall. BaTiO<sub>3</sub> which will be formed on the other hand if heating temperature is too low or the Ba/Ti ratio in early stages of growth is not suitable A film becomes the orientation instead of orientation (110) made into the purpose (001), or (001) it is orientation BaTiO<sub>3</sub>. An orientation (110) crystal will be intermingled on a film. BaTiO<sub>3</sub> which supplied Ba reacts with the zirconium-oxide system thin film of a ground in early stages of growth, and has the target orientation It is hard to be obtained. Suppose that Ti is superfluous in early stages of growth for avoiding the reaction of Ba and a zirconium oxide. In addition, thickness is within the limits which is about 1nm or less the early stages here of growth.

[0124] About various conditions, such as oxygen tension the membrane formation speed at the time of insulating ground thin film formation, the kind of oxidizing gas, its amount of supply, and near the substrate, and rotation of a substrate, it is the same as that of the case of the above-mentioned zirconium-oxide system thin film formation.

[0125] As well as the case of the above-mentioned ferroelectric thin film since it can enforce the above-mentioned formation method of a middle thin film or an insulating ground thin film especially in comparison with the conventional vacuum deposition method, the sputtering method, the laser abrasion method, etc. under the operating condition which does not have the room of an intervention of an impurity so that clearly and which is moreover easy to control, it is suitable to obtain the specified substance with good repeatability and high integrity by the large area. Even if it uses MBE equipment in the above-mentioned method, the target thin film can completely be obtained similarly.

[0126] When it constitutes from a conductive ground thin film metal, forming by vacuum evaporation is desirable. As for the substrate temperature at the time of vacuum evaporation, it is desirable to consider as 500-750 degrees C. If substrate temperature is too low, a crystalline high film will not be obtained, but if substrate temperature is too high, the irregularity of a membranous front face will become large. In addition, crystallinity can be further raised by introducing Rf plasma, passing the oxygen of a minute amount in a vacuum tub at the time of vacuum evaporation. There is an effect which specifically prevents orientation (111) mixing into orientation (001) in Pt thin film.

[0127] When it constitutes from the oxide or the conductive perovskite oxide containing In, it is desirable to use the above-mentioned formation method of a ferroelectric thin film or an insulating ground thin film, in addition it can also use reactant plural vacuum depositions and a spatter.

[0128] About the ferroelectric thin film in the ferroelectric thin film film structure, it is desirable to form by the above-mentioned manufacture method of a ferroelectric thin film.

[0129]

[Example] Hereafter, the concrete example of this invention is shown and this invention is further explained to a detail.

[0130] Pt (001) orientation film was formed in the front face of cutting and the single crystal MgO disk (diameter of 2 inches) which carried out mirror polishing by the vacuum deposition, and it considered as the substrate so that a <example 1> front face might turn into a field (100), and the ferroelectric thin film

was formed in the following procedures on this substrate.

[0131] First, the above-mentioned substrate was fixed to the substrate electrode holder equipped with the rotation and the heating mechanism which were installed in the vacuum tub, and the vacuum tub was exhausted to 10<sup>-6</sup>Torr with the oil diffusion pump.

[0132] Subsequently, a substrate is heated at 600 degrees C and it is 20rpm. It was made to rotate. And the Pb-Gd-Ti multiple-oxide film (PGT thin film) of 300nm of thickness was formed by introducing radical oxygen gas at ten cc a rate for /from the source of efficient consumer response oxygen, and evaporating PbO, TiOx, and (x= 1.67) Gd from each evaporation source on a substrate. The supply from an evaporation source is PbO:Gd:TiOx. It carried out controlling so that a mole ratio is set to 2:0.1:1. That is, it was referred to as E (Pb/Ti) = 2.0.

[0133] When X-ray fluorescence investigated composition of the formed PGT thin film, it was (Pb+Gd)/Ti=1.02 and Pb/(Pb+Gd)=0.90. In this composition, since it is set to F (Pb/Ti) = 0.92, it is set to E (Pb/Ti) / F (Pb/Ti) = 2.2.

[0134] Evaluation by RHEED was performed about this PGT thin film. The RHEED pattern of this PGT thin film is shown in drawing 2 . The direction of incidence of the electron ray at this time was made into the [110] directions of a MgO substrate. As this result shows, the diffraction pattern of this PGT thin film front face is a pattern which is completely a streak. From this pattern and X diffraction evaluation, it has checked that the formed PGT thin film was a perovskite structure, and was an epitaxial film of c plane orientation. Moreover, it crosses throughout a surface simultaneously about this film, and they are ten places and JIS. When the ten-point average of roughness height Rz (a criteria length of L:500nm) by B0610 was measured, it was [ on the average / in 6.3nm and the maximum ] as flat as 1.3nm at 9.0nm and the minimum.

[0135] Cutting, and single crystal Si [ p type 5ohm ] disk of specific resistance (cm) (diameter of 2 inches) which carried out mirror polishing were used for the substrate so that a <example 2> front face might turn into a field (100). The front face which carried out mirror polishing performed etching washing by ammonium-fluoride solution 40%. It is ZrO2 by the procedure shown in the front face of this substrate below. A thin film (middle thin film) and BaTiO3 The thin film (insulating ground thin film) and the ferroelectric thin film were formed in this order. In addition, although an X diffraction and RHEED estimated each thin film, the sample with which evaluation was presented is taken out in the middle of a series of thin film formation processes in a vacuum tub, respectively. Also in the following examples, it is the same.

[0136] First, it is 20rpm about the substrate after fixing the above-mentioned substrate to the substrate electrode holder equipped with the rotation and the heating mechanism which were installed in the vacuum tub and exhausting a vacuum tub with an oil diffusion pump to 10<sup>-6</sup>Torr. It heated at 600 degrees C, having made it rotate and introducing oxygen near a substrate front face at 25 cc a rate for /from a nozzle. This formed Si oxide layer with a thickness of about 1nm.

[0137] Subsequently, 900 degrees C was made to heat and rotate a substrate. A rotational frequency is 20rpm. It carried out. Si surface treatment substrate equipped with the surface structure of 1x1 was obtained by supplying Zr from an evaporation source, introducing oxygen gas at 25 cc a rate for /from a nozzle at this time. The amount of supply of Zr was set to 5nm by thickness conversion of Zr oxide.

[0138] Next, it is ZrO2 of 10nm of thickness by supplying Zr from an evaporation source, where oxygen gas is introduced at 25 cc a rate for /from a nozzle, the substrate temperature of 900 degrees C, substrate rotational frequency 20rpm, and. The thin film was formed on the aforementioned processing substrate, and it considered as the middle thin film.

[0139] It is this ZrO2 as a result of an X diffraction. In a thin film, only a reflective (00L) peak is accepted, and the half-value width of a reflective (002) rocking curve is 0.7 degrees, and it turns out that it is the single orientation and the film of high crystallinity which are not in the former. In addition, although the peak (002) had lapped with Si (200) peak originating in a substrate, the above-mentioned half-value width is a value including Si (200) peak.

[0140] Furthermore, when RHEED measurement was performed about this thin film, the diffraction pattern on the front face of a thin film is a pattern which is completely a streak, and has checked that this



thin film was an epitaxial film from this pattern that is completely a streak. When  $R_z$  was measured like [ thin film / this ] the above, it is 0.08nm in 1.00nm and the minimum on an average at 0.80nm and the maximum, and it turns out on molecule level that it is flat.

[0141] In addition,  $ZrO_2$  It is  $ZrO_2$  when the stabilized-zirconia thin film was formed instead of the thin film. The same crystallinity as a thin film and front-face nature were obtained. Moreover,  $ZrO_2$  It is  $ZrO_2$  as a result of measuring the resistivity of the zirconium-oxide (YSZ) thin film stabilized by the thin film and Y. The thin film showed 5 times as much high resistance as a YSZ thin film, and excelling in insulation was checked.

[0142] Next, it is  $BaTiO_3$  of 50nm of thickness by supplying Ti from an evaporation source at a rate of Ba and 1:1, where a nozzle to the substrate temperature of 900 degrees C, substrate rotational frequency 20rpm, and oxygen gas are introduced at 25 cc a rate for /. It is a thin film  $ZrO_2$  It formed on the thin film and considered as the insulating ground thin film.

[0143] This  $BaTiO_3$  When the X diffraction was performed about the thin film, only the peak (00L) was accepted and it has checked that the half-value width of a reflective (002) rocking curve was 1.4 degrees, and was the film of the high crystallinity in single (001) orientation.

[0144] When RHEED measurement of this thin film was carried out, a diffraction pattern is a pattern which is completely a streak, and it was checked that it is an epitaxial film.

[0145] Si substrate and  $ZrO_2$  A thin film and  $BaTiO_3$  The result of the X diffraction of each thin film which each orientation relationship of a thin film described above showed that they were  $BaTiO_3$  / (001) /  $ZrO_2$  / (001) / Si (100). Moreover, as a result of performing RHEED measurement about each thin film as fixed in the direction of incidence of an electron ray, it is these RHEED measurement to  $BaTiO_3$ .

[100] //  $ZrO_2$  It has checked that they were [100] // Si [010].

[0146] Next, the PGT thin film of 300nm of thickness was formed like the example 1.

[0147] When X-ray fluorescence investigated composition of the formed PGT thin film, it was  $(Pb+Gd)/Ti=1.01$  and  $Pb/(Pb+Gd)=0.89$ . In this composition, since it is set to  $F(Pb/Ti) = 0.90$ , it is set to  $E(Pb/Ti) / F(Pb/Ti) = 2.2$ .

[0148] Evaluation by RHEED was performed about this PGT thin film.

[0149] The RHEED pattern of this thin film is shown in drawing 3 . The direction of incidence of the electron ray at this time was made into the [110] directions of Si substrate. As this result shows, a RHEED pattern is a pattern which is completely a streak. From this pattern and X diffraction, it has checked that the formed PGT thin film was a perovskite structure, and was an epitaxial film of c plane orientation. Moreover, when  $R_z$  was measured like the above, it was [ on the average ] as flat as 0.9nm at 7.5nm and the minimum in 3.0nm and the maximum.

[0150] Pt electrode was formed in this PGT thin film front face, and it considered as MFIS structure. this -- the inside of the atmosphere -- setting -- 750 degrees C -- annealing during 10 minutes -- aluminum electrode of OMIKKU was formed in the substrate rear face the back the bottom, and the C-V property was evaluated A result is shown in drawing 4 . The hysteresis characteristic is obtained as shown in drawing 4 . a hysteresis band -- about 0.8 -- V it was . Next, this property was used and the element which used the ferroelectric thin film for the gate oxide film of FET was produced. It is 0.7V, when the gate voltage of FET was changed and the current between the source and a drain was measured. The memory window was obtained and non-volatile memory operation was checked. It was the the best for the gate type non-volatile memory which have MFIS structure to the dielectric constant of a PGT thin film being about 200, and ferroelectric thin films, such as the conventional PZT, being about 1000 since it is small.

[0151] On the same single crystal Si substrate as the <example 3> example 2, it is  $ZrO_2$ . A thin film (middle thin film) and  $BaTiO_3$  The thin film (insulating ground thin film), Pt thin film (conductive ground thin film), and the ferroelectric thin film were formed in this order.

[0152]  $ZrO_2$  A thin film and  $BaTiO_3$  The thin film was formed like the example 2.

[0153] Subsequently,  $BaTiO_3$  The substrate which has a thin film on a front face was heated at 700 degrees C, and Pt thin film of 100nm of thickness was formed by the vacuum deposition method. It is 100W, introducing oxygen gas at three cc a rate for /, in order to prevent mixing of Pt (111) on the

occasion of formation of Pt thin film. Rf plasma was introduced.

[0154] About this thin film, as a result of an X diffraction and RHEED estimating, it was checked that it is the epitaxial film of single (001) orientation.

[0155] Next, the PGT thin film with a thickness of 300nm was formed like the example 1.

[0156] When X-ray fluorescence investigated composition of the formed PGT thin film, it was  $(\text{Pb}+\text{Gd})/\text{Ti}=1.07$  and  $\text{Pb}/(\text{Pb}+\text{Gd})=0.90$ . In this composition, since it is set to  $F(\text{Pb}/\text{Ti})=0.96$ , it is set to  $E(\text{Pb}/\text{Ti})/F(\text{Pb}/\text{Ti})=2.1$ .

[0157] About this PGT thin film, RHEED evaluation was performed like the example 2. The obtained RHEED pattern is shown in drawing 5. Moreover, the X diffraction view of this PGT thin film is shown in drawing 6. In drawing 6, since only the c-th plane reflective peak of the perovskite structure of PGT was detected and the streak pattern was accepted in drawing 5, it was checked that this thin film is an epitaxial film of single (001) orientation.

[0158] Next, it is  $\text{ZrO}_2$  on Si substrate like the above. A thin film and  $\text{BaTiO}_3$ . After carrying out the laminating of a thin film and the Pt thin film, the ferroelectric thin film containing the rare earth elements shown in Table 1 was formed, and the membrane structure object sample was obtained. On the occasion of formation of these ferroelectric thin films, it was  $E_{\text{SUB}}(\text{Pb}/\text{Ti})/F(\text{Pb}/\text{Ti})=1.9-2.2$ . The abbreviated-name displays (PGT etc.) of the kind of ferroelectric thin film of each sample were shown in Table 1. In addition, in Table 1, the sample which has the above-mentioned PGT thin film is also indicated. Moreover, for comparison, it is the same structure and the sample which has a lead-titanate (PT) thin film as a ferroelectric thin film was also produced. Moreover, in order to perform comparison by the substrate, the sample which has PT thin film or a La addition PT (PLT) thin film on the substrate {the substrate which has Pt (001) orientation film on  $\text{MgO}$ } used in the example 1 was also produced. Composition of the ferroelectric thin film of each sample is shown in Table 1.

[0159] According to the X diffraction, the ferroelectric thin film of this invention sample is a perovskite crystal, orientation and orientation (100) were intermingled in sample No.14 (PPT thin film) (001), and it has checked that it was single orientation (001) with other this invention samples. Moreover, the RHEED pattern of the ferroelectric thin film of this invention sample was a streak-like. Therefore, it turns out that a crystallographic axis is very good and the ferroelectric thin film of sample No.14 has gathered within a film surface although orientation (001) and orientation (100) are intermingled, and it turns out that the ferroelectric thin film of other this invention samples is an epitaxial film.

[0160] The RHEED pattern and X diffraction view of a ferroelectric thin film of sample No.7 (PTT thin film) are shown in drawing 8 and drawing 11, and the RHEED pattern and X diffraction view of a ferroelectric thin film of sample No.8 (PDT thin film) are shown for the RHEED pattern and X diffraction view of a ferroelectric thin film of sample No.2 (PPT thin film) in drawing 7 and drawing 10 at drawing 9 and drawing 12, respectively.

[0161] sample No.2 [ moreover, ] (PPT thin film) -- the inside of the atmosphere -- setting -- 750 degrees C -- annealing during 10 minutes -- a next X diffraction view is shown in drawing 13 the bottom Comparison with drawing 10 and drawing 13 shows that the orientation (100) crystal appeared by annealing.

[0162] the ferroelectric thin film front face of each sample -- Pt electrode of 0.11mmphi -- forming -- the inside of the atmosphere -- setting -- 750 degrees C -- annealing during 10 minutes -- the bottom, the back, the lead was taken out from Pt thin film which is a conductive ground thin film, and the D-E hysteresis was measured by radiographic66A (radiant TEKINO logy company make) Consequently, the hysteresis was acquired with all this invention samples, and the ferroelectric polarization property was shown. It represents and the hysteresis curve of sample No.2 (PPT thin film), sample No.6 (PGT thin film), and sample No.7 (PTT thin film) is shown in drawing 14, and 15 and 16, respectively. Moreover, the resistivity of the ferroelectric thin film which shows the remanence value  $P_r$ , the anti-electric field (polarization turn over voltage)  $E_c$ , and the leak property of each sample, and the polarization reversal fatigue property were measured. A result is shown in Table 1. In addition, a polarization reversal fatigue property is 106. Bias 0V after repeating batch pole reversal Polarization value  $P_r$  1 Early polarization value  $P_r$  0 The ratio ( $P_r1 / P_r0$ ) showed. The value of a fatigue property becomes small, so that



degradation by polarization reversal is intense.

[0163]

[Table 1]

サンプル No.	種類	希土類 元素Rn	(Pb+Rn)/Ti (μ比)	Pb/(Pb+Rn) (μ比)	抵抗率 (Ωcm)	2Ec (V)	2Pr (μC/cm <sup>2</sup> )	疲労特性 (%)
本発明例 (S i 基板)								
1	PLT	La	1.03	0.89	$2.02 \times 10^{11}$	2.9	29	72
2	PPT	Pr	1.00	0.92	$1.01 \times 10^{11}$	2.8	30	75
3	PNT	Nd	1.08	0.88	$5.25 \times 10^{10}$	3.3	49	60
4	PST	Sm	1.06	0.91	$1.43 \times 10^{11}$	4.1	48	63
5	PET	Eu	1.13	0.91	$1.40 \times 10^{11}$	4.9	59	65
6	PGT	Gd	1.07	0.90	$6.56 \times 10^{10}$	4.2	41	70
7	PTT	Tb	1.02	0.91	$8.57 \times 10^{10}$	3.7	23	80
8	PDT	Dy	1.16	0.88	$1.70 \times 10^{11}$	2.7	8.6	80
9	PHT	Ho	1.03	0.91	$3.48 \times 10^{10}$	3.9	26	79
10	PErT	Er	1.15	0.87	$8.50 \times 10^{10}$	2.7	6.8	90
11	PVbT	Yb	1.11	0.90	$3.03 \times 10^{10}$	1.8	3.0	90
12	PVT	Y	1.11	0.86	$9.32 \times 10^{10}$	2.5	8.5	90
13	PPGT	Pr, Gd	1.06	0.90	$1.02 \times 10^{11}$	2.8	31	76
14	PPT	Pr	1.02	0.96	$3.86 \times 10^{10}$	4.4	57.8	62
15	PPT	Pr	1.06	0.83	$6.49 \times 10^{11}$	0.9	4.5	78
比較例 (S i 基板)								
16	PT	なし	1.06	1.0	$1.99 \times 10^{10}$	6.2	60	45
比較例 (MgO 基板)								
17	PT	なし	1.01	1.0	リーク	測定不能	測定不能	測定不能
18	PLT	La	1.03	0.89	リーク	測定不能	測定不能	測定不能

[0164] this invention sample which has the ferroelectric thin film which added predetermined rare earth elements has succeeded in lowering Ec effectively compared with the comparison sample which has the lead-titanate thin film which has not added rare earth elements so that clearly from Table 1. Moreover, it turns out that this invention sample excels the comparison sample in the leak property and the defatigation property. Moreover, when the ferroelectric thin film which added La is formed on a MgO substrate, it turns out that leak is intense and a ferroelectric property is not acquired.

[0165] Although the dielectric constant of PT thin film (sample No.16) of the example of comparison shown in Table 1 was 510, the dielectric constants of the ferroelectric thin film of this invention sample shown in Table 1 were 196-626, and the low dielectric constant was fully obtained for the following [equivalent to PT thin film].

[0166] In addition, even when other metal thin films, such as Ir thin film, were used as an electric conduction ground thin film, the same result as the above was obtained.

[0167] Moreover, it is ZrO<sub>2</sub> as a middle thin film. Even when what carried out the laminating of a thin film and the rare earth oxide thin film was used, the same result as the above was obtained.

[0168] Moreover, when applied to the record medium which mentioned above the membrane structure object produced in the above-mentioned example, the record reproduction by the AFM probe was possible.

[0169]

[Effect of the Invention] The ferroelectric thin film in this invention consists of lead system ferroelectric

material which added predetermined rare earth elements, and can be applied to non-volatile memory, an infrared sensor, an optical modulator, optical-switch OEIC, a record medium, etc. by using the outstanding ferroelectric property. It is the the best for the record-medium use which records with the gate type non-volatile memory which has MFIS structure and MFMIS structure especially, and probes, such as AFM.

[0170] The manufacture method of this invention is the operating condition which enables realization of the thin film which has the outstanding ferroelectric property, and does not have the room of mediation of an impurity and which is easy to control, and can form a quality lead system ferroelectric thin film with sufficient repeatability over a large area with a diameter of 2 inches or more. And it is what enabled production of such a thin film on Si substrate which is a semiconductor application overlay important point, and utility value is industrially high.

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[Translation done.]

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## CLAIMS

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### [Claim(s)]

[Claim 1] It is the membrane structure object characterized by providing the following, and a ferroelectric thin film is R1 (R1). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, and Er, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of  $(\text{Pb}+\text{R1})/\text{Ti}=0.8-1.3$  and  $\text{Pb}/(\text{Pb}+\text{R1})=0.5-0.99$ . The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled. Substrate. The ferroelectric thin film formed on this substrate.

[Claim 2] The membrane structure object of a claim 1 with which the ferroelectric thin film is formed in the aforementioned front-face side of the substrate which has Si (100) side on a front face.

[Claim 3] It is the membrane structure object characterized by providing the following, the front face by the side of the ferroelectric thin film of a substrate has Si (100) side, and a ferroelectric thin film is R2 (R2). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, Er, and La, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of  $(\text{Pb}+\text{R2})/\text{Ti}=0.8-1.3$  and  $\text{Pb}/(\text{Pb}+\text{R2})=0.5-0.99$ . The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled. Substrate. The ferroelectric thin film formed on this substrate.

[Claim 4] It is one membrane structure object of the claims 1-3 which it has an insulating ground thin film between a substrate and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, are single (001) orientation when it is a tetragonal phase, and are single (100) orientation when it is a cubic.

[Claim 5] It is the membrane structure object of the claims 1-3 which it has a middle thin film between a substrate and a ferroelectric thin film, and this middle thin film makes a principal component the zirconium oxide by which this zirconium-oxide system thin film was stabilized by a zirconium oxide or rare earth elements (Sc and Y are included) including the zirconium-oxide system thin film, are single (001) orientation when it is a tetragonal phase or monoclinic system, and are single (100) orientation when it is a cubic.

[Claim 6] It is the membrane structure object of the claim 5 which this rare earth oxide system thin film exists [ a middle thin film ] between a zirconium-oxide system thin film and a ferroelectric thin film including a rare earth oxide system thin film, and this rare earth oxide system thin film makes a principal component the oxide of rare earth elements (Sc and Y are included), is single (001) orientation when it is a tetragonal phase or monoclinic system, and is single (100) orientation when it is a cubic.

[Claim 7] It is the membrane structure object of the claims 5 or 6 which it has an insulating ground thin film between a middle thin film and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, are single (001) orientation when it is a tetragonal phase, and are single (100) orientation when it is a cubic.

[Claim 8] In contact with a ferroelectric thin film, it has a conductive ground thin film. this conductive ground thin film It is the conductive oxide thin film which consisted of oxides which have the oxide or the perovskite type crystal structure containing the conductive metal thin film which consisted of at least

one sort of Pt, Ir, Os, Re, Pd, Rh, and Ru, and/or In. It is one membrane structure object of the claims 1-7 which are single (001) orientation when it is a tetragonal phase, and are single (100) orientation when it is a cubic.

[Claim 9] One membrane structure object of the claims 1-8 whose ten-point averages of roughness height  $R_z$  with a criteria length of 500nm are 10nm or less in at least 80% of field of a ferroelectric thin film front face.

[Claim 10] One membrane structure object of the claims 1-9 with which below 60 atom % of Ti in a ferroelectric thin film is replaced by at least one sort of Zr, Nb, Ta, Hf, and Ce.

[Claim 11] The electron device which has one membrane structure object of the claims 1-10.

[Claim 12] The record medium which has one membrane structure object of the claims 1-10.

[Claim 13] The manufacture method of the ferroelectric thin film which performs vacuum evaporation while facing the ferroelectric thin film which consists of an oxide which contains Pb and Ti at least forming on a substrate by plural vacuum depositions and introducing a oxidizing gas in a vacuum evaporation reaction chamber at least, using a lead oxide and  $TiO_x$  ( $1 \leq x \leq 1.9$ ) as an evaporation source.

[Claim 14] It is the atomic ratio of the element supplied from an evaporation source  $Pb/Ti=E$  ( $Pb/Ti$ ) It is an atomic ratio in the ferroelectric thin film which were formed by carrying out  $Pb/Ti=F$  ( $Pb/Ti$ ) The manufacture method of the ferroelectric thin film of a claim 13 set to  $E(Pb/Ti)/F(Pb/Ti)=1.5-3.5$  when it carries out.

[Claim 15] The manufacture method of the ferroelectric thin film of claims 13 or 14 using the oxygen which at least the part radical-ized as a oxidizing gas.

[Claim 16] The manufacture method of one ferroelectric thin film of the claims 13-15 which make temperature of a substrate 500-700 degrees C, and perform vacuum evaporation.

[Claim 17] The manufacture method of one ferroelectric thin film of the claims 13-16 that the ferroelectric thin film containing at least one sort of Zr, Nb, Ta, Hf, and Ce is formed.

[Claim 18] The manufacture method of one ferroelectric thin film of the claims 13-17 applied to manufacture of one membrane structure object of the claims 1-10.

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[Translation done.]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is drawing showing an example of the vacuum evaporation equipment used for the manufacture method of the ferroelectric thin film of this invention.

[Drawing 2] It is the drawing substitution photograph in which the crystal structure is shown, and is the RHEED pattern of the PGT thin film formed on Pt (001) thin film formed on the MgO (100) substrate. The direction of incidence of an electron ray is the MgO [100] direction.

[Drawing 3] It is the drawing substitution photograph in which the crystal structure is shown, and is the RHEED pattern of the PGT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].

[Drawing 4] It is the C-V property of MFIS structure using the PGT ferroelectric thin film.

[Drawing 5] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PGT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].

[Drawing 6] Pt(001)/ It is the X diffraction view of the PGT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 7] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PPT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].

[Drawing 8] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PTT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].

[Drawing 9] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PDT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].

[Drawing 10] Pt(001)/ It is the X diffraction view of the PPT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 11] Pt(001)/ It is the X diffraction view of the PTT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 12] Pt(001)/ It is the X diffraction view of the PDT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 13] It is an X diffraction view after annealing of the PPT thin film of drawing 10.

[Drawing 14] Pt(001)/ It is the D-E hysteresis characteristic of the PPT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 15] Pt(001)/ It is the D-E hysteresis characteristic of the PGT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 16] Pt(001)/ It is the D-E hysteresis characteristic of the PTT thin film formed on BaTiO<sub>3</sub>/(001)ZrO<sub>2</sub> / (001) Si (100) structure.

[Drawing 17] (a) is the \*\* type view showing the RHEED pattern of the surface structure of 1x1, and (b)

is the \*\* type view showing a RHEED pattern in case 2x1, 1x2, or these are intermingled.

[Description of Notations]

1 Vacuum Evaporation Equipment

1a Vacuum tub

2 Substrate

3 Electrode Holder

4 Axis of Rotation

5 Motor

6 Heater

7 Oxidizing Gas Feeder

8 Oxidizing Gas Feed Hopper

9 PbO Evaporator

10 TiO<sub>x</sub> Evaporator

11 Rare-Earth-Elements Evaporator

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[Translation done.]

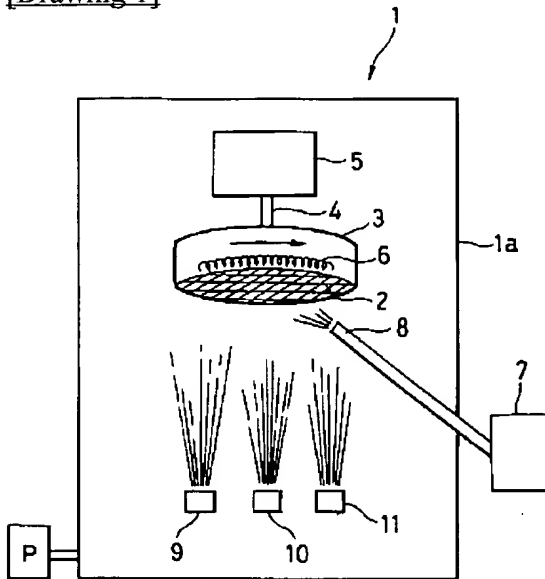
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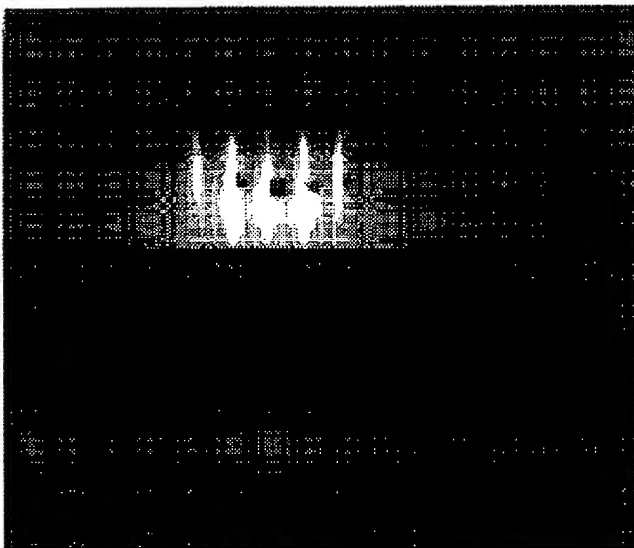
## DRAWINGS

[Drawing 1]



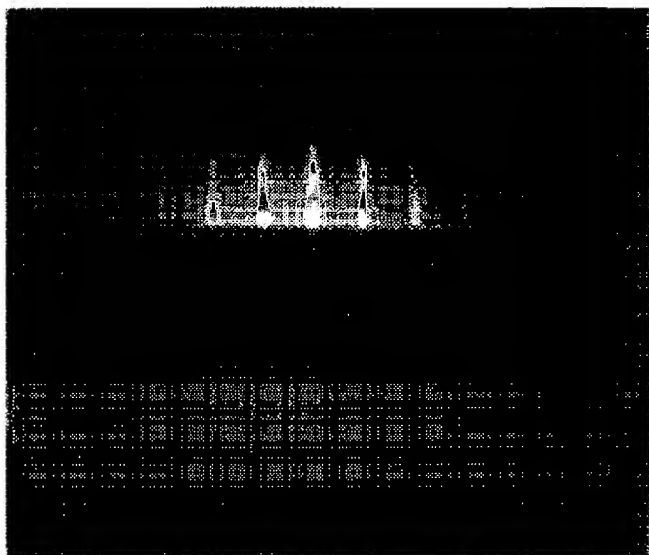
[Drawing 2]

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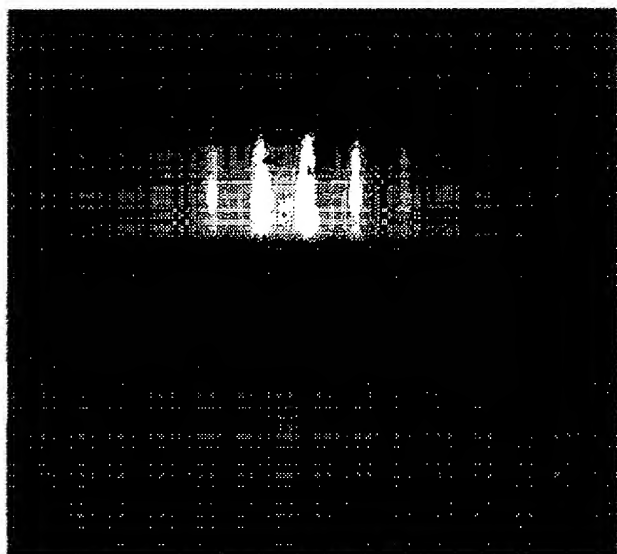
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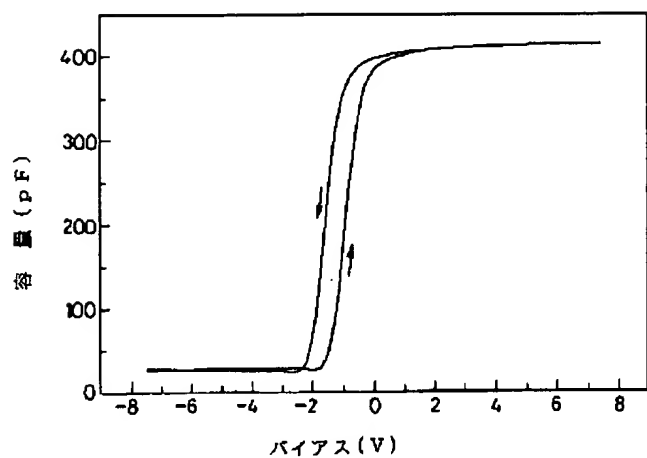
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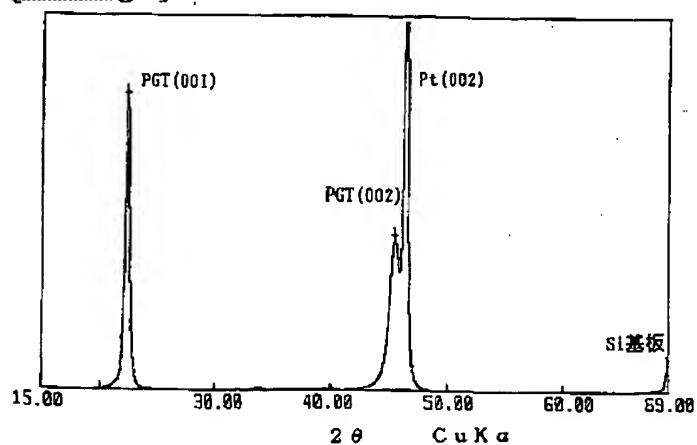


[Drawing 4]



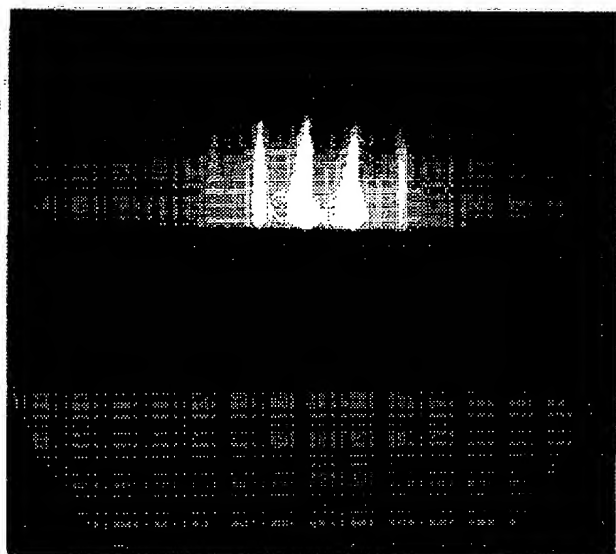


[Drawing 6]



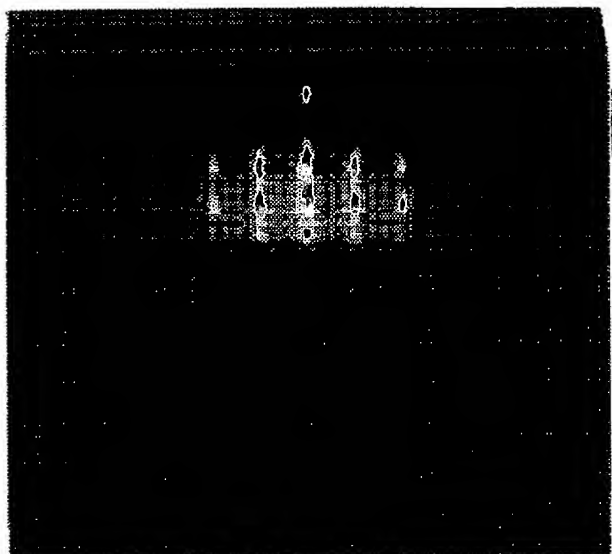
[Drawing 7]

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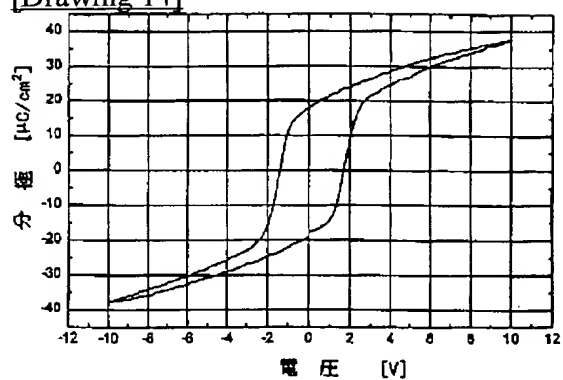


[Drawing 8]

図面代用写真

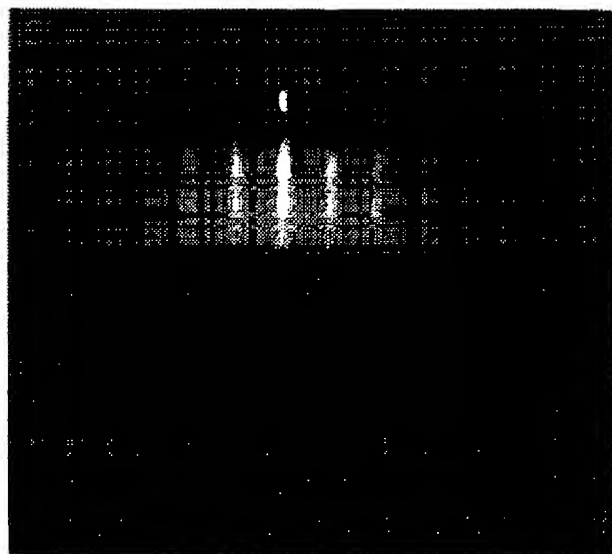


[Drawing 14]

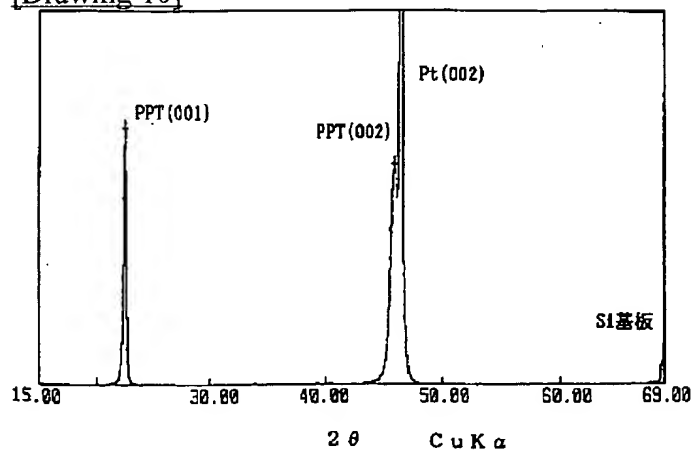


[Drawing 9]

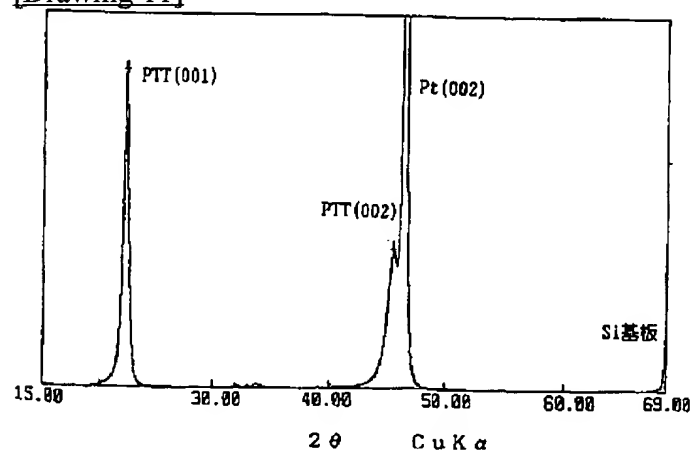
図面代用写真



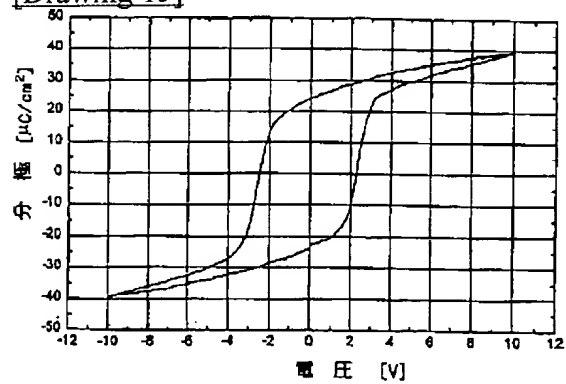
[Drawing 10]



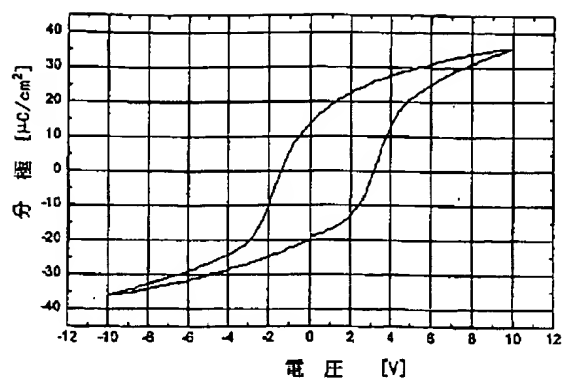
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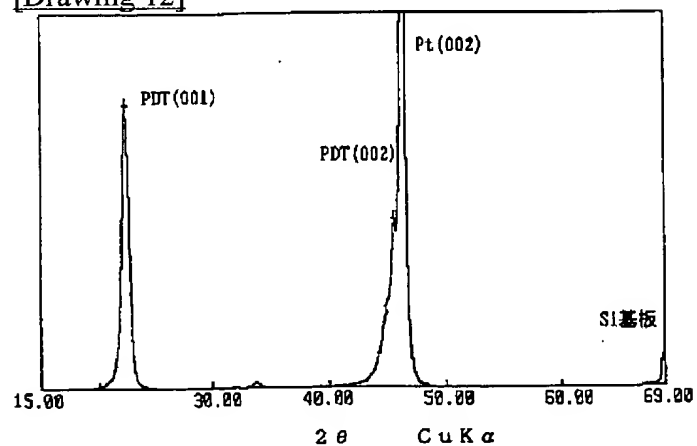
[Drawing 15]



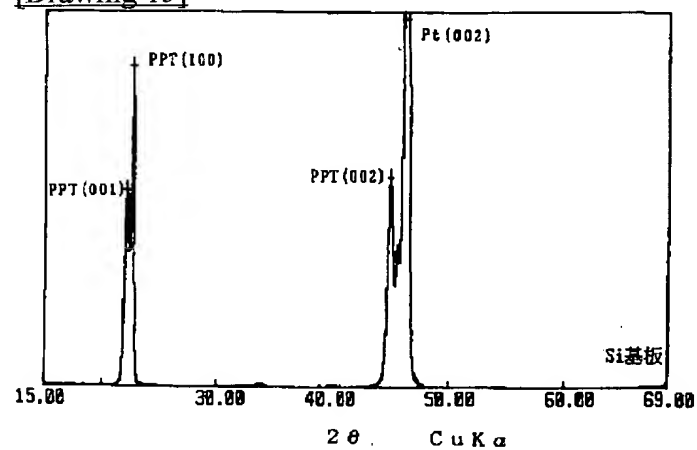
[Drawing 16]



[Drawing 12]



[Drawing 13]



[Drawing 17]